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Modern Methods to Measure Air Pollutants

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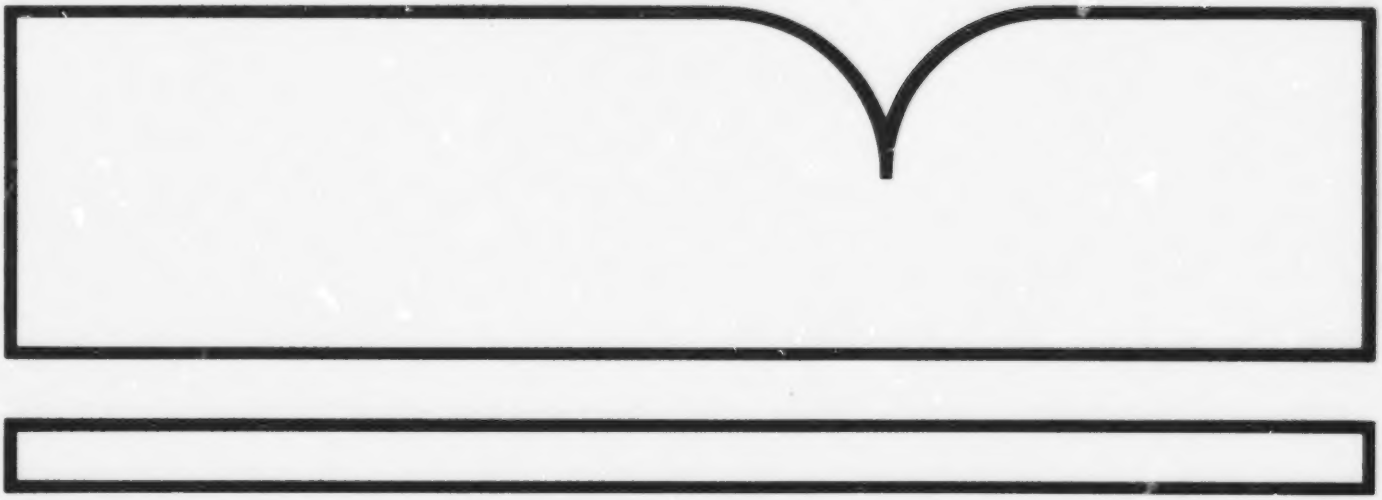

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MODERN METHODS TO MEASURE AIR POLLUTANTS

Robert K. Stevens

U. S. Environmental Protection Agency
Research Triangle Park, North Carolina, U.S.A.

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT

This paper discusses the requirements for the collection and analysis of ambient particles to satisfy data requirements for source and receptor models as applied to pollution control applications. The paper describes the following analytical procedures as applied to receptor modeling: X-ray fluorescence (XRF), neutron activation (NAA), ion exchange chromatography (IC), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM) as well as the recent application of gas phase denuders to measure a wide range of pollutants, including nitric acid and ammonia.

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Abstract

The atmosphere is an enormously complex mixing vessel. And yet, in spite of that complexity the aerosol particles found there retain distinctive distributions with respect to size and composition. The bimodal size distribution for aerosols has been found in various regions by many investigators, and analysis of the particle size fractions has shown that the two modes differ considerably in their elemental constituents and in their chemistry. For example, the fine particle fraction is often acidic; and the coarse particle fraction, is often basic. This interesting dichotomy is consistent with the view that the fine particle fraction is constituted largely of particles formed from atmospheric gases, and that among these gases are the acidic oxides of sulfur and nitrogen. On the other hand, the coarse particle fraction is mainly composed of crustal elements, among which are the metals Ca and K, which form the basic oxides. In practice, our primary interest in measuring the chemical properties of particles is to provide information for pollution control. Two complementary orientations exist to address pollution control issues. One approach, termed 'receptor modeling', begins with the measurements of elemental abundances in particles collected downwind of the sources and works back through a model to determine the contribution of those sources to the particulate mass loading. The second approach, termed 'source' or 'dispersion modeling', is based on a continuity (conservation) equation describing material in the atmosphere, and uses source emission rates, meteorological parameters, rates of transport, and transformation data to calculate the expected air quality. The test of the validity of these model calculations is the agreement of the predicted values

with experimental observations of air quality. This paper discusses the requirements for the collection and analysis of ambient particles to satisfy data requirements for source and receptor models as applied to pollution control applications. The paper describes the following analytical procedures as applied to receptor modeling: X-ray fluorescence (XRF), neutron activation (NAA), ion exchange chromatography (IC), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM) as well as the recent application of gas phase denuders to measure a wide range of pollutants, including nitric acid and ammonia.

Introduction

The atmosphere is an enormously complex, more or less effective, mixing vessel. And yet, in spite of that complexity (numerous sources, sinks, transport processes, and transformations), the aerosol particles found there retain distinctive distributions with respect to size and composition. The bimodal size distribution for aerosols* has been found in various regions by many investigators, and analysis of the particle size fractions has shown that the two modes differ considerably in their elemental constituents and in their chemistry. For example, the fine particle fraction is often acidic; and the coarse particle fraction is often basic. This interesting dichotomy is consistent with the view that the fine particle fraction is constituted largely of particles formed and accreted from atmospheric gases, and that among these gases are the acidic oxides of sulfur and nitrogen.** On the other hand, the coarse particle fraction is mainly formed from the larger particles breaking up, among which are certain metals (Ca, K), which form the basic oxides. These properties of atmospheric particles are schematically represented in Figure 1.

In general, we find that the elements sulfur and lead appear mostly in the fine fraction, and calcium, aluminum, and silicon appear mostly in the

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* Aerosol particles will be referred to as "aerosols", not to be confused with gas and solids or liquids.

** The relative contribution of nitrogen oxides to particle formation is now a controversial subject, and evidence exists that previous estimates were considerably too high.

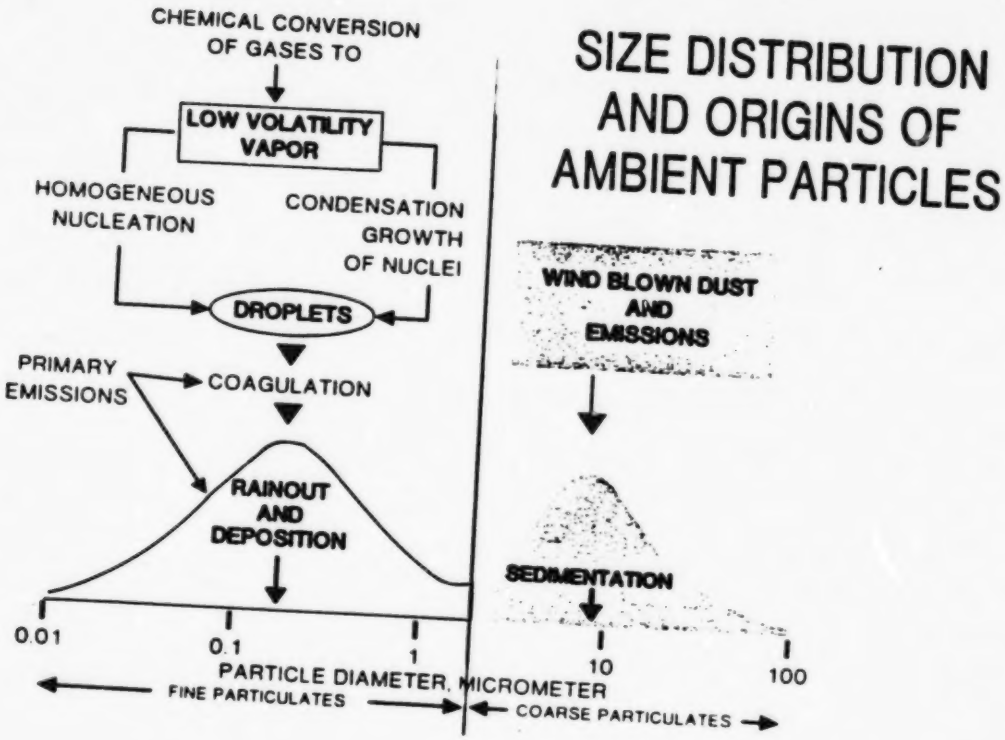


Figure 1. Size distribution and origins of ambient particles.

coarse fraction. These elements, which usually appear in quantities measured in micrograms per cubic meter, are not thought of as trace elements.

In practice, EPA's primary interest in measuring materials in the atmosphere is to provide information for pollution control. Two complementary orientations to this problem exist. In "source apportionment models," one begins with the measurements of elemental abundances in particles collected downwind of the sources and works back through a model to determine the contribution of those sources to the particulate mass loading. In "air quality simulation models," one takes a continuity (conservation) equation describing material in the atmosphere and various input and output data (source emission rates, meteorological parameters, rates of transport and transformation, etc.) and calculates the air quality. The test of the model calculation is the agreement of its predicted values with experimental observations of air quality. Experimental determinations of elements in atmospheric particles are necessary, then, in both approaches to the assignment of atmospheric sources: one approach works from the observations back to the source, and the other work from the source to the observations. These remarks are illustrated in Figure 2.

The following sections of the paper discuss the requirements for the collection and analysis of ambient particles to determine the mass and elemental composition and to determine the physical properties and chemical species present in the sample. The choice of sampling equipment and characterization procedures for ambient particles for environmental study data collection should be dictated by the objectives of the study. In the case of determining the effects of aerosols on surfaces, the identification and the physical and chemical properties of as many of the components that constitute the aerosol sample should be an integral part of the study.

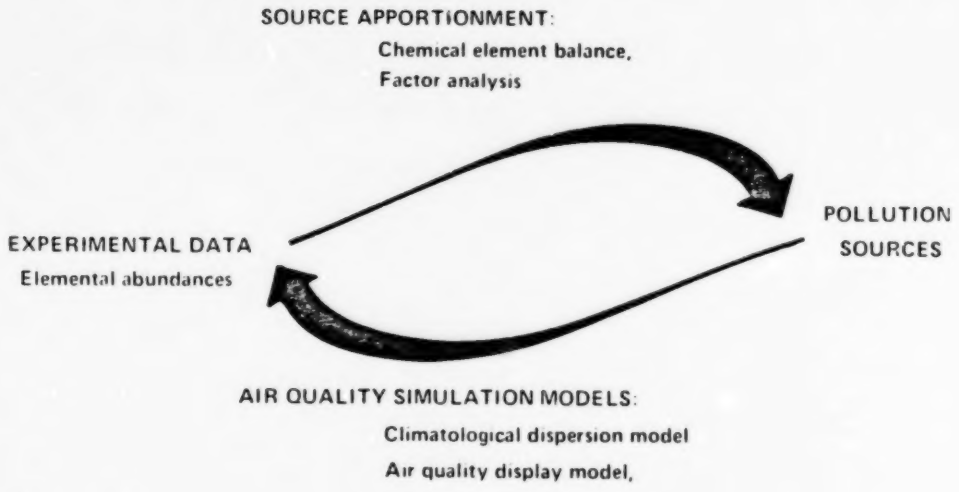


Figure 2. Model paths connecting experimental measurements of elements in atmospheric particles and the source of those particles.

The discussion that follows also describes the procedures and the application of the following instrumental methods for particle characterization: X-ray fluorescence (XRF), neutron activation analysis (NAA), ion exchange chromatography (IC), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM). Also, the procedure for and application of gas phase denuders to measure HNO_3 and nitrate and a combustion method to measure the carbon content of particles will be described.

From this array of analytical procedures, the chemical and physical properties of ambient particles are determined and their potential impact on man and materials can be inferred. In addition, the sources of the ambient particles can frequently be identified from these same chemical properties, e.g., elemental composition is used as input to receptor models (1).

SAMPLERS AND FILTER MEDIA

Of the many aerosol sampling methodsin use today, no one method can provide the range of measurements necessary for the comprehensive chemical analysis required in many air quality environmental impact studies. In this discussion of samplers and filter media, we assume that particle collection will be made over 24 hour periods and that particles <2.5 μm in diameter (fine fraction) and the particles > 2.5 μm in diameter (coarse fraction) are of interest and will be collected and analyzed. In addition, we will assume the need to measure chemical and physical properties of each of these fractions and for both inorganic and organic content.

Dichotomous Sampler: One particle collection system that has been used frequently by the U.S. Environmental Protection Agency (EPA) to provide

samples compatible with the above discussed requirements is the dichotomous sampler. This sampler is designed to use either Teflon or quartz filters that satisfy another important requirement in aerosol characterization studies: the sample collection will be nearly free from artifact formation. Table 1 contains a list of commonly used filter types and their respective properties. Note the alkalinity of the glass fiber filters, responsible for sulfate artifacts during sampling.

Table 1. Properties of filters used to collect ambient particulate samples.

SUMMARY OF USEFUL FILTER PROPERTIES

FILTER AND FILTER COMPOSITION	DENSITY mg/cm^2	pH	FILTER EFFICIENCY %*
TEFLON (MEMBRANE) $(CF_2)_n$ (2μm PORE SIZE)	0.5	NEUTRAL	99.95
CELLULOSE (WHATMAN 41) $(C_6H_{10}O_5)_n$	8.7	NEUTRAL (REACTS WITH HNO_3)	58% AT 0.3 μm
GLASS FIBER (WHATMAN GF/C)	5.16	BASIC pH - 9	99.0
"QUARTZ" GELMAN MICRO—QUARTZ	6.51	pH · 7	98.5
POLYCARBONATE (NUCLEPORE) $C_{15}H_{14}CO_3$ (0.3μmPORE SIZE)	0.8	NEUTRAL	93.9
CELLULOSE ACETATE/NITRATE MILLIPORE (1.2μm PORE SIZE) $(C_9H_{13}O_7)_n$	5.0	NEUTRAL (REACTS WITH HNO_3)	99.6

*MINIMUM EFFICIENCY FOR PARTICULATE DIAMETER >0.035μm AT V = 10cm/sec

Sampling artifacts are defined as the chemical reactions of acidic gases with certain types of filters to form nonvolatile species, e.g., $SO_2 + M \rightarrow SO_4M$ or $HNO_3 + M \rightarrow MNO_3$; where M is a metal impurity (e.g., Na, Ca) in the collection substrate. Thus, the true sulfate and nitrate concentration is perturbed by this artifact. Glass fiber filters and cellulose membrane filters are notorious for producing sulfate and nitrate artifacts (2).

The dichotomous sampler is a virtual impactor that aerodynamically separates particles into size fractions corresponding to the fine and coarse modes of the normal size distribution of ambient particles and deposits the particles uniformly on the filters. A schematic diagram of the dichotomous sampler is shown in Figure 3. More detailed diagram of the inertial impactor separation stage is shown in Figure 4. Ambient particles should be collected on 1 or 2 μm pore size Teflon filter (3) if the elemental composition is to be determined accurately by XRF or ionic content (4). Teflon filters are the filter medium of choice because they are inert, chemically pure, and have a high collection efficiency, as noted in Table 1. The density of 2 μm pore size membrane Teflon filter is approximately 500 $\mu g/cm^2$. This low density is ideal for XRF and mass measurements while having > 99% collection efficiency for particles > 0.05 μm in aerodynamic diameters. However, quartz filters are used for condensable carbon measurements in field studies because total condensable carbon content is typically measured by a thermal combustion procedure described by Huntzicker et al. (5). This combustion procedure will be discussed in detail in the measurement section of this report.

Cyclone Samplers: In field studies where only the fine particles (<2.5 μm) are to be collected, cyclone inlets can be used to remove the coarse particles. Figure 5 is an example of a typical sampling system that uses a

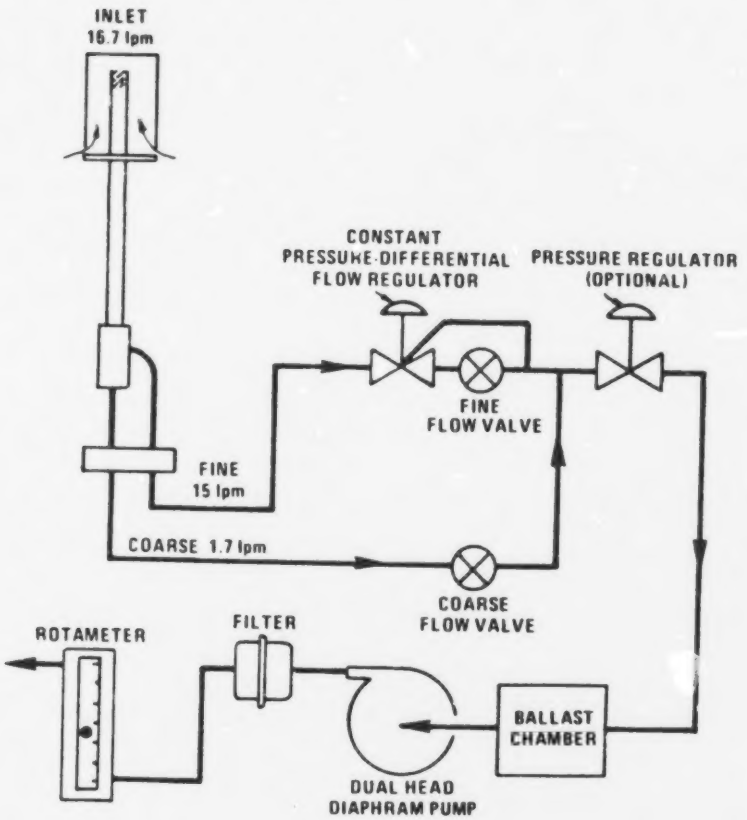


Figure 3. Diagram of Dichotomous Sampler System

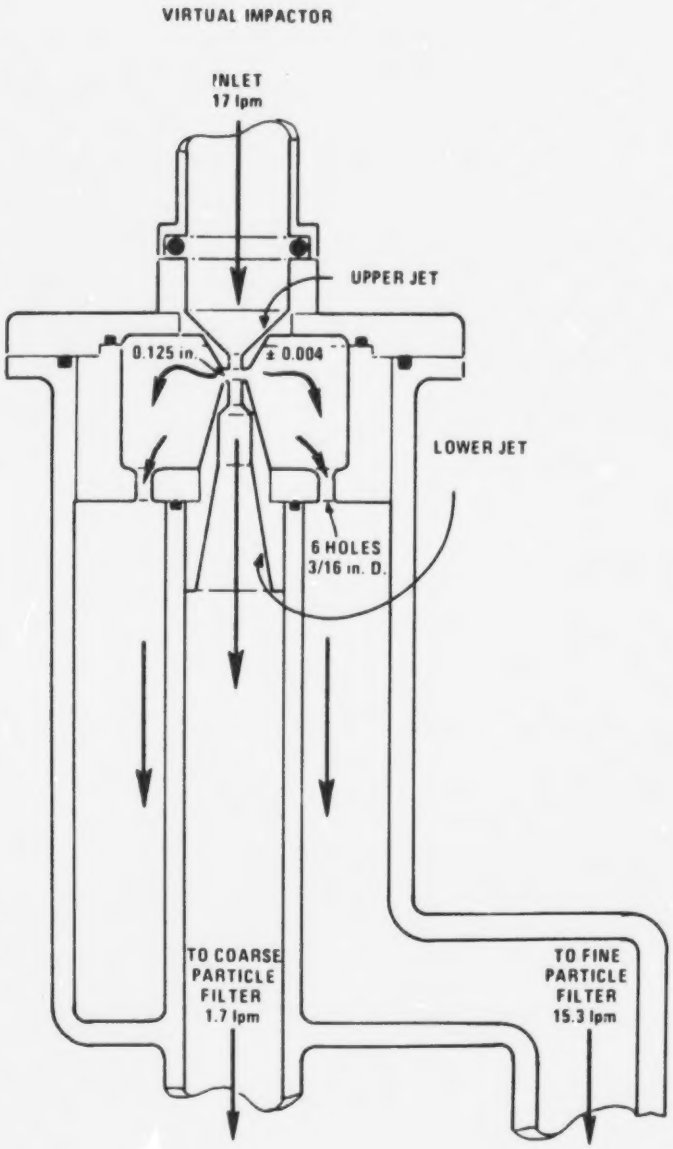


Figure 4. Diagram of Virtual Impactor

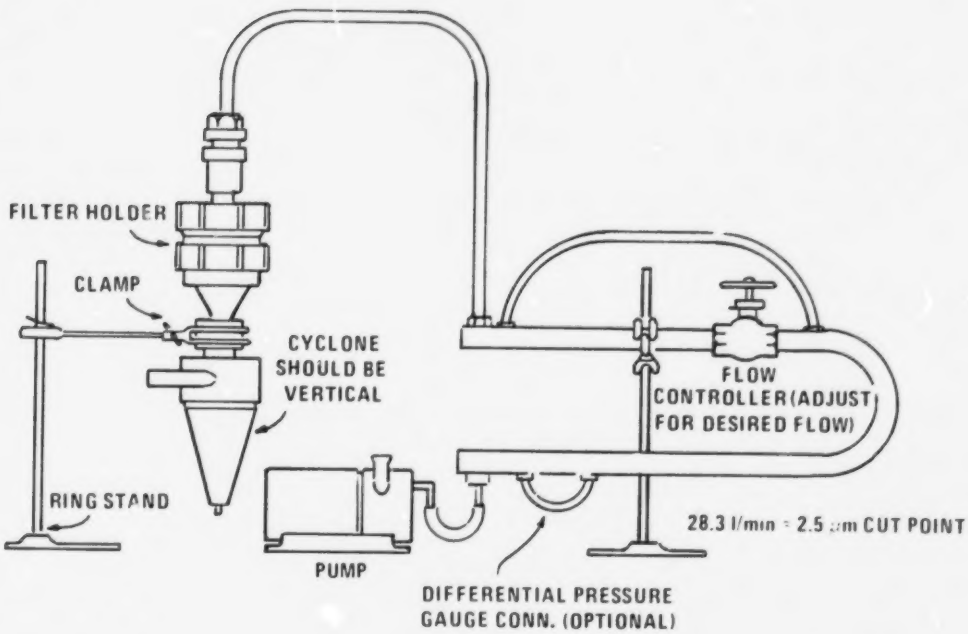


Figure 5. Schematic of fine particle sampler with cyclone inlet and pneumatic flow controller.

cyclone inlet, pneumatic flow controller, pump, and filter and particle collection assembly. This aerosol collection arrangement samples the air and deposits the fine particles onto a 37 mm diameter filter. One of the advantages of using cyclone inlets when collecting particles is that a variety of sample flow rates and cutpoints can be used by selecting the appropriate cyclone design. Also, Lippmann and Chase (7) noted that cyclone samplers can be designed to match respiratory deposition curves. John and Reischl (6) have recently described the properties of several cyclones that would be applicable to air pollution monitoring studies.

ANALYSIS

Mass: The mass of the aerosol collected can be measured by gravimetric procedures. Typically, the mass of aerosol collected on a 37 or 47 mm diameter Teflon filter can be determined to within ± 25 μg per filter. Therefore, if 24 m^3 of ambient air is pulled through a filter and the average particle content is 50 $\mu g/m^3$, the mass of particulates collected on the filter can be measured to a precision of ± 2%. For some studies performed by the EPA, mass measurements are made by β-ray attenuation using a method characterized by Jaklevic et al. (8) and Courtney et al. (9). The β-ray attenuation and gravimetric procedures can both determine the mass of aerosol collected on Teflon filters to ± 25 μg. Measurements of mass collected on quartz filters are not as accurate because the quartz is extremely fragile and the weight is difficult to obtain in a micro-balance.

Elemental Composition: There are a number of analytical procedures that can be used to measure the elemental content of aerosols. Some of these methods require that the sample be extracted and then analyzed by an emission

spectrographic procedure. For example, Scott et al. (10) reported multi-element analysis of about one thousand Hi-vol filters by low temperature oxygen ashing and followed by acid extraction of the filter and analysis of the extract by optical emission spectroscopy (OES). Their paper also provides considerable information on detection limits and confidence levels determined by extensive replicate and standard sample analysis. The absolute sensitivity of OES is not as high as that of some other techniques. The Hi-vol sampler, however, collected so much sample that OES was sufficiently sensitive to provide quantitative determinations of Al, Be, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ti, and V in a set of 898 samples from 248 sites in the National Air Surveillance Network (NASN). Determinations were also made of As, Bi, Co, Bs, Sn, Te, and Tl, but the levels were above the detection limit in fewer than 1% of the samples. Table 2 shows the frequency of detection, which is defined as the percentage of samples in which the element is detected at a level above the detection limit. Scott et al. (10) defined the detection limit as the concentration corresponding to a signal three times the standard deviation above the average signal due to the extraction solution. The extraction solution contained internal standards for normalization of measured values.

It is clear from Table 2 that OES analysis of the NASN samples has provided sufficient data to follow trends in abundances of Cu, Fe, Mn, Pb, and Ti, but certainly not As, Bi, Co, Sb, Sn, Te, or Tl, and probably not Mo. Whether sufficient data exist for Al, Be, Ca, Cd, Cr, Mg, Ni, and V depends on more detailed considerations, e.g., comparisons of element levels with detection limits, interelement interferences, and the requirements of the statistical treatment of the data. Obviously, these results refer only to the 1970 NASN samples; samples from different sites will probably have different frequencies of detection.

Table 2
Frequency of detection by OES of elements in NASN samples.

Number of Samples: 898
Sampling Period: 1970
Sampler and Flow Rate: Hi-vol, 1.7 m^3/min

Element	Frequency of Detection
Cu, Fe, Mn, Pb, Ti	80-100%
Al, Be, Ca, Cd, Cr, Mg, Ni, V	10-80%
Mo	< 10%
As, Bi, Co, Sb, Sn, Te, Tl	< 1%

For many recent air pollution studies, energy dispersive x-ray fluorescence analysis (EDXRF) has been widely used to analyze nondestructively the elemental composition of ambient particles. Stevens et al. (4) used calibration procedures described below to measure the elemental content of ambient particles. The x-ray machine used in these studies was fabricated by Lawrence Berkeley Laboratory and uses a pulsed x-ray tube to excite a secondary target which, in turn, excites the sample with nearly non-energetic x-rays (11).

To obtain high sensitivity for a wide range of elements, each sample is excited by means of three different secondary targets. For the K x-rays of elements with atomic numbers in the ranges 13-20, 21-38, and 39-56, the secondary targets consist of titanium, molybdenum, and samarium, respectively. The molybdenum target also excites the L x-rays of lead and other heavy elements. The fluorescent x-rays from the sample are detected using a lithium drifted silicon detector, that uses electronic collimation to minimize the background. Because of a compact geometrical arrangement between components of the spectrometer, an x-ray tube power of only 100 W is sufficient to provide the maximum usable count rate for filter samples.

After a sample has been irradiated in the EDXRF spectrometer, the resulting spectrum is analyzed to determine the number of counts that each element contributes. To accomplish this, a least-squares procedure is used to find a linear combination of single-element spectra that best describes the unknown spectrum. A library of single-element spectra is obtained for thin standards of each element and is stored in computer memory. The library must contain all elements that could contribute to an unknown sample (4, 11, 12, 13).

The least-squares method is slightly modified for the K x-rays from sulfur to deal with the overlapping M x-rays from lead. Because the concentration of lead can be accurately determined from the emission of L x-rays, it is possible to 'strip' out the interfering lead M peak in the vicinity of the sulfur peak. Such stripping is done prior to performing the least-squares analysis for sulfur. The uncertainty in the result for sulfur due to the presence of lead is estimated to be about 5% of the lead concentration. For example, if the lead concentration were 2 $\mu g\ m^{-3}$, the resulting sulfur uncertainty would be 0.1 $\mu g\ m^{-3}$. The complete description of the calibration of the EDXRF system is described by Stevens et al. (4).

For most air pollution applications in which only the major elements are needed to determine elemental content of a particulate sample, EDXRF is adequate. However, EDXRF cannot be used to accurately determine elements lighter than Al, or routinely observe the various minute trace elements such as Lu, Hf, Ta, W, Th, Sm, Dy, Yb, Se, As, and La.

A particularly useful combination is EDXRF followed by instrumental neutron activation analysis (INAA). The latter technique, described by Kowalczyk et al. (14) is totally instrumental and, depending on mass loadings and filter blanks, can observe up to 40 elements. Gordon et al. (15)

demonstrated the value of applying INAA to samples from the Regional Air Pollution Study that had previously been subjected to XRF. These studies show that the combination of XRF and INAA yielded data for 28 elements in the fine fraction and 32 in the coarse fraction for virtually every sampling period. An additional 18 elements in the fine fraction and 14 in the coarse fraction were observable in about half of the samples. Furthermore, 11 elements (Al, Ca, K, Cl, Ti, V, Mn, Fe, Zn, Br, and Ba) can usually be measured by both methods for a quality assurance check. Thorough INAA requires access to a reactor with a flux of at least 10^{13} n cm^{-2}-s^{-1} and a high-resolution Fe (Li) or intrinsic Ge γ-ray spectrometry system. Irradiations of two different lengths are needed for species of various half-lives (see below).

As presently performed, compared with XRF, INAA requires considerably more sample handling, interpretation of results, longer analytical time (2-3 weeks after irradiation for certain long-lived isotopes), for the resolution of certain elements (S + Pb), and, consequently, is considerably more costly per sample. Thus, XRF is often the preferred screening technique. All samples could be subjected to XRF and the results used to identify only the most interesting samples for further analysis by INAA.

Another way to reduce INAA cost is an approach taken by Watson (16) and Core et al. (17) at the Oregon Graduate Center. Complete INAA requires at least two irradiations of samples: the first for a few minutes to observe species with half-lives of $\leq$15 h, and the second for several hours to observe species with half-lives of up to several years. The former method is less costly to perform, as the γ-ray spectra are simple enough to be resolved primarily by computer. Furthermore, in the former, results are usually available within a day after the irradiation, compared with about three weeks after irradiation for long-lived isotopes. The Oregon Graduate Center group

has employed INAA cost effectively by performing only the short irradiation following XRF analyses. Depending on the conditions, most of the following elements are usually observed: Na, Mg, Al, S, Cl, K, Ca, Ti, V, Mn, Cu, Br, La, Sm, Dy, and W. However, some important elements that are normally observed in long irradiations (Cr, Co, As, Se, and Bs) are usually sacrificed in this approach.

Many other techniques are used to observe elements in atmospheric particulate matter, including atomic absorption spectrophotometry, inductively coupled plasma atomic emission spectrometry, spark-source mass spectrometry, various electrochemical methods (such as anodic stripping voltammetry), and chemical separations followed by colorimetry. Most require considerable labor per sample to obtain accurate results or (unlike EDXRF and INAA) require dissolution of samples prior to analysis. Moreover, any chemical manipulation greatly increases the chance of contamination by trace elements and loss of volatile or insoluble species.

Ionic Species: The major ionic species present in ambient particles are sulfate ($SO_4^=$), nitrates (NO_3^-), hydrogen (H^+), chlorides (Cl^-), bromide (Br^-) and ammonium (NH_4^+). After EDXRF analysis, samples may then be extracted and the anion and cation concentration measured. The extraction process used when analysis of particles collected on Teflon filters is required consists of removing the filter from its holder, loading it into an extraction vessel, filling the vessel with extraction solution, and then extracting by the use of an ultrasonic bath.

The filters are carefully removed from the filter holders and as quickly as possible placed into the extraction solution in order to prevent contamination. For acidity measurements, care must be taken not to breathe on

the filters in order to minimize exposure to exhaled ammonia. The filters are placed in the extraction vessel with the back of each filter facing the bottom in order to prevent any material from being inadvertently removed as the filter is inserted into the vessel.

The extraction vessel recommended is a 30-ml Nalgene polypropylene bottle (Nalge, Inc., Rochester, NY) that has been conditioned by soaking in extraction solution for at least 8 h before use. To keep the filter submerged and open during extraction, a fluted Teflon pipe is placed in the vessel so that the fluted end rests on the outer, unloaded edge of the filter.

The volume of extraction solution used depends on the type and number of analyses performed and ranges from 8 to 20 ml. The extraction solution, perchloric acid, is diluted to 5×10^{-5} N with distilled water. The extraction solution is delivered with 0.05% precision to the vessel by an Oxford Laboratories macro set pipet. The vessel is then capped and placed in an ultrasonic bath (Model 8845-60, Cole-Palmer Instrument Co., Chicago, Illinois) for 20 min. The ultrasonic bath tends to produce standing waves in the water so that regions exist where no agitation takes place. To overcome this problem, the extraction vessel is continuously moved during the extraction period.

The above extraction procedure is used for analysis of $SO_4^{=}$, NO_3^{-}, NH_4^{+} and H^{+}. For the fine and coarse particle fractions, Stevens et al. (3) found the extraction efficiencies for sulfur to be 98 ± 1% and 95 ± 2%, respectively.

For those samples on which a sulfite determination is to be made, the extraction procedure is modified to minimize the conversion of sulfite to sulfate. Stevens et al. (4) demonstrated that carrying out the extraction at room temperature caused complete conversion of sulfite to sulfate. To prevent such conversion, a cold extraction process was developed. In the modified

procedure, the water bath was made up of a slurry of ice and water that maintained the temperature of the sample at 0°C during the extraction. With this procedure 90% of the sulfite was preserved.

Hydrogen ion analysis Titrimetry and a Gran's function plot are recommended to determine strong acidity using the procedure of Brosset and Ferm (18). The instrumentation includes an Orion pH meter, a combination electrode, a Gran's function generator, and a Radiometer autoburett ABU 12. The data can be recorded on a 1-mV strip-chart recorder. The Gran's function generator is an antilog amplifier (Model 755, Analog Devices, Norwood, MA).

The acid analysis procedure is as follows: 1) standardization of sodium hydroxide titrant, 2) measurement of the concentration of the acid extraction solution, 3) titration of extract using the 0.001 N NaOH, and 4) data analysis. Steps 1 and 2 are done once for each set of filter extracts or at least once each day. Nitrogen is bubbled through the solution being titrated to remove an interference by CO_2. The ionic strength of the volume being titrated is maintained at 0.02 M by the addition of KCl.

The method has been characterized by performing 50 measurements on sulfuric acid standards that had a range of concentrations. The linear dynamic range was 10^{-6} to 10^{-4} M. The relative standard deviation was 2% and the minimum detectable level was 1 nano-equivalent ml^{-1} (neq m^{-1}).

Ion exchange chromatography: Ion exchange chromatography is a relatively new technique for routine analysis of anions and cations in aqueous extracts of ambient aerosols. Mulik et al. (19) has described the application of a commercial liquid IC (Dionex Model 14, Sunnyvale, CA) to the analysis of water soluble anions. Before injecting a sample into the IC, 5 ml of the aerosol

extract is spiked with the IC eluent (typically 1:1 mixture of 0.003 M Na_2CO_3 and 0.0024 M $NaHCO_3$) to adjust the molar CO_3^- concentration to the range of 10^{-3} to 10^{-5}. This basic mixture is then added to neutralize the minute concentrations of perchloric acid used in the extraction procedure so that the injected solutions are approximately the molar concentration of the eluent used in the chromatograph. Because the instrument calibration curve is not linear, multi-point calibrations are performed over the range of concentrations expected in the samples. The signal from the IC conductivity detector can be processed by a Hewlett Packard 3385A chromatographic control system. Peak areas and retention times are recorded to quantify and identify specific anions.

Typical relative standard deviations for mixtures of sodium nitrate and ammonium aqueous sulfate standards are shown in Table 4. Retention times and relative standard deviations were determined daily. The minimum detectable levels for sulfates and nitrates were 10^{-1} neq ml^{-1} and 5×10^{-2} neq ml^{-1}, respectively. A typical IC chromatogram of an extract of a fine particle sample collected in Philadelphia is shown in Fig. 6. Note the low nitrate concentration as compared to sulfate. For almost all aerosol samples collected with the dichotomous sampler using Fluoropore filters, nitrate was always a small fraction of the sulfate concentration.

Table 3. Relative standard deviations for IC analysis of nitrate and sulfate standards.

Molarity	Dionex attenuation setting	Standard deviation* SO_4^-	Standard deviation* NO_3^-
1×10^{-4}	10	1%	1%
5×10^{-5}	10	0.3%	1%
1×10^{-5}	3	1.6%	1%

* Based on four consecutive injections of 0.4-ml volumes of standard solutions.

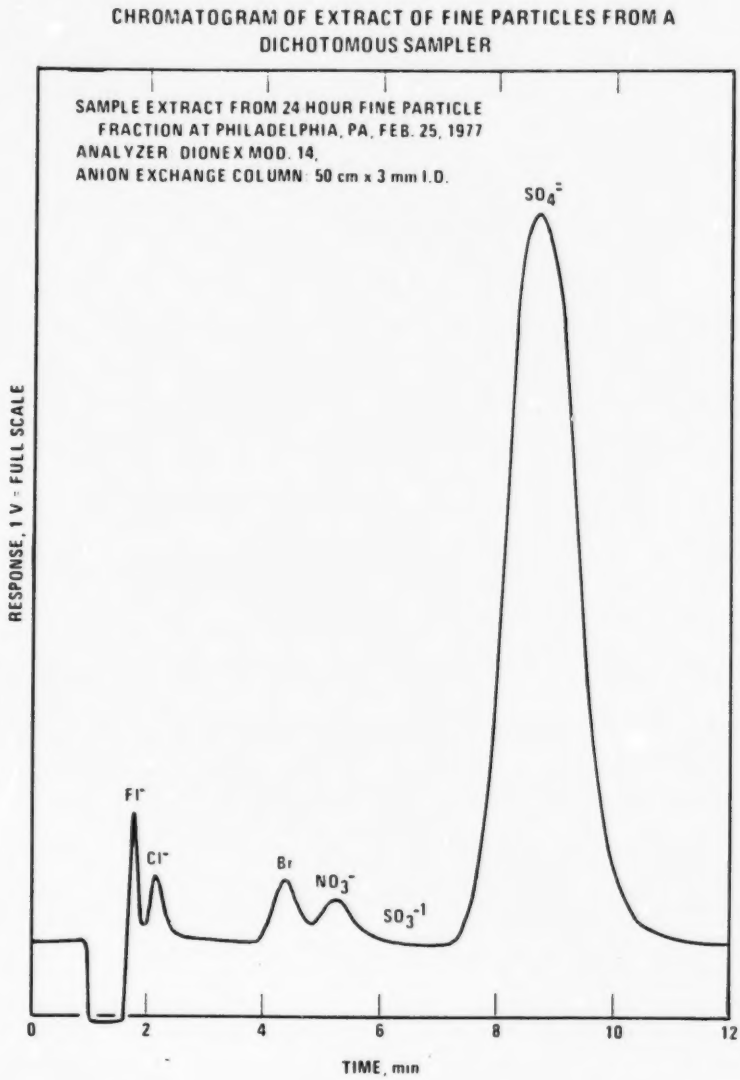


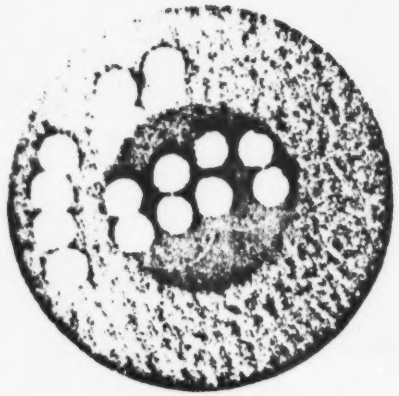
Figure 6. Ion chromatogram of anion content of fine particle sample collected in Philadelphia, PA.

Ammonium analysis: The concentration of ammonium ions may be determined with an ion selective NH_3 gas diffusion electrode (Orion Model 95-10). The response is recorded from a Corning-Digital 112 pH meter. Analysis is performed by mixing 7 ml of filter extract and 0.2 ml of 5 N sodium hydroxide in a 20-ml glass beaker. The electrode is immersed into the solution with the tip extending approximately 1 cm into the solution. Readings are made between 2 and 3 min. after immersing the electrode into the extract. When the sample concentration is less than 1×10^{-5} M, equilibration required as long as 5 min. The electrode is calibrated using dilute NH_4Cl standards (10^{-2} to 10^{-6} M). The minimum detectable level is 3 neq ml^{-1}. At concentrations above 10 neq ml^{-1}, the relative standard deviation is typically ± 5%. Recently Abbas and Tanner (20) developed a technique which measures ambient levels of ammonia. The method is based on measuring the intense fluorescence of the reaction product of NH_3 and a thio-mecaptan in solution. The method measures continuously NH_3 at sub-ppb concentrations.

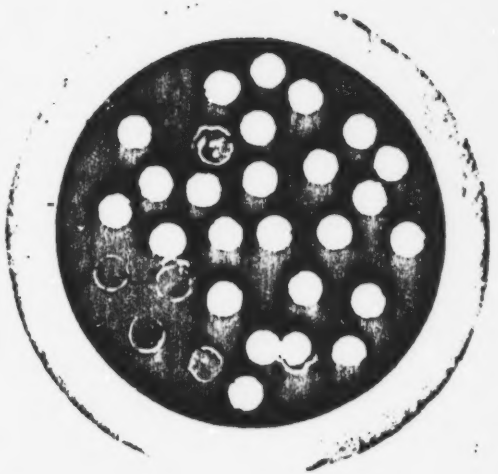
Carbon Measurements and Radioisotopic Analysis of $^{14}C/^{12}C$: Stevens et al. (4) have documented the basis for using Teflon filter substrates to obtain mass measurements and perform XRF analyses for elemental composition. However, carbon measurements are not easily obtained from Teflon filters, because the procedure used most frequently to measure carbon in aerosols is based on high-temperature combustion methods. For this reason, a second fine particle sample must be collected on quartz at the same time the aerosols are being collected on Teflon. Quartz is used as the collection medium because it has a low carbon content, high collection efficiency, and is chemically inert. An aliquot of the quartz filter can be analyzed by a combustion procedure similar to one described by Stevens et al. (20). This procedure measures volatile

carbon and elemental carbon from the same sample. Recent comparisons of methods by Cadle et al. (21) to measure elemental, total and volatile carbon content of aerosols indicate that procedures that depend on combustion or pyrolysis to convert the carbon species into methane followed by flame ionization measurement, may produce substantially different results, depending on the conditions for combustion. For example, to convert completely all the aerosol carbon on quartz filters requires a temperature of at least 850°C and the presence of oxygen in the helium carrier gas. Without oxygen, a substantial amount of elemental carbon will not be pyrolyzed and consequently will not be measured.

At the present time, we measure the elemental and condensable carbon present in ambient particulate samples using a modified Dohrmann DC-50 organic analyzer (DC-50). Figure 8 is a diagram depicting the sample introduction, pyrolysis, combustion and detector assemblies. The DC-50 measures the organic carbon (condensable organics) by pyrolyzing the carbonaceous portion of the sample to CO_2 and other pyrolysis products at 650°C in a helium atmosphere reduces the products to methane over a bed of nickel catalyst in an atmosphere of hydrogen, and measures the methane with a flame ionization detector. After the organic analysis, elemental carbon is determined by combustion of the carbonaceous materials remaining on the quartz filter at 850°C in a 2% oxygen, 98% helium atmosphere. Total carbon is considered to be the sum of the organic and elemental analysis. Recently, we have modified the procedure to collect particles on quartz filters in order to minimize the variations in the blanks. The modification reduces the deposit area of the sample from 37 mm to 13 mm, as shown in Figure 7. This focusing of the sample to a 13 mm area reduces the impact of the carbon blank and the area outside the deposit area becomes the blank for that filter. The combination of increased sample per



A



B

FINE PARTICLE SAMPLES COLLECTED ON QUARTZ FILTERS.

SAMPLE A. COLLECTED BY MODIFYING SAMPLE FLOW TO FOCUS AEROSOLS INTO A 13 mm SPOT. THIS PROVIDES A HIGH DENSITY OF SAMPLE PER UNIT AREA AND REDUCES BLANK UNCERTAINTIES.

SAMPLE B. COLLECTED NORMALLY IN DENVER, CO, JAN., 1982. THE HOLES IN THE FILTERS ARE WHERE PIECES WERE REMOVED FOR CARBON ANALYSIS.

Figure 7. Fine particles samples collected on quartz filters.

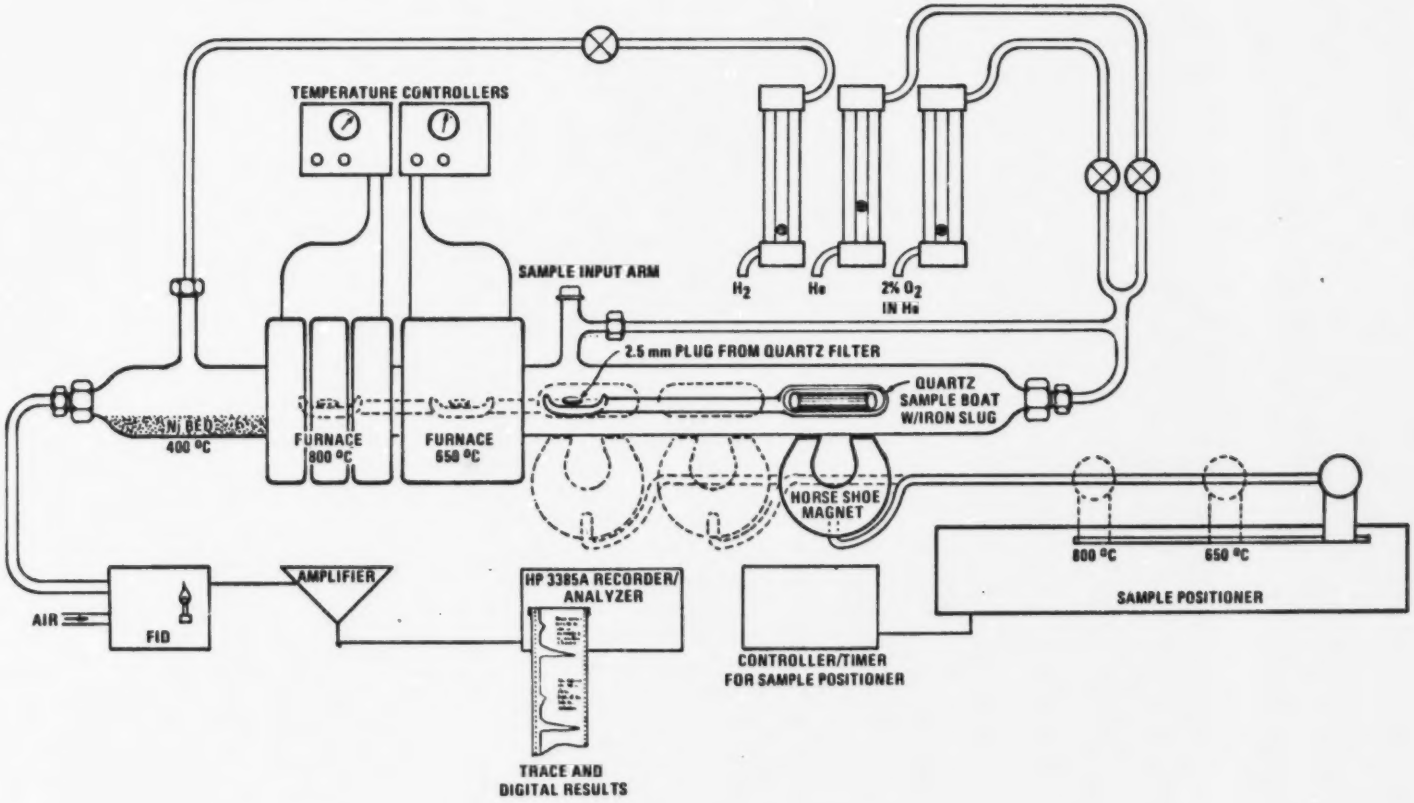


Figure 8. Diagram of modified Dorhmann DC-50 elemental and organic carbon analyzer.

unit area and a blank for each sample should improve the precision of the combustion procedure to determine carbon content of aerosols.

Currie (22) determined the relative amounts of particulate carbon from contemporary and fossil fuel carbon combustion sources by means of data on the $^{14}C/^{12}C$ ratio. The distinction is possible because contemporary carbon contains trace amounts of ^{14}C, but fossil fuel carbon is essentially devoid of ^{14}C. The $^{14}C/^{12}C$ measurements are relatively expensive and only two or three laboratories in the U.S are capable of performing the analysis. In addition, milligram amounts of material are needed to measure $^{14}C/^{12}C$ in ambient particulate samples. Currie (23) is currently working on a new procedure that measures ^{14}C with an accelerator mass spectrometer at the University of Arizona. With this new system, as little as 100 μg carbon may be analyzed.

The National Bureau of Standards (NBS) normally measures $^{14}C/^{12}C$ by heating the quartz or glass fiber filters to distill the condensable organics from the filters; the organics are then converted to CO_2 and the CO_2 is condensed into a glass microcell. The cell is placed into a sealed chamber and the radioactivity is measured with a sensitive proportional counter. Recently, Stevens et al. (24) reported the presence of carbonates, acetate and formate in aqueous extracts of ambient fine particles collected in the Shenandoah Valley of Northern Virginia, U.S.A. Stevens et al. postulated these species may interfere with ^{14}C measurements, because the carbonate may result from CO_2 adsorption on the quartz filter. Because almost all of the ambient CO_2 is rich in ^{14}C, the bulk ^{14}C analysis described above may be influenced by the CO_2 artifact formed with the quartz filter. For this reason the improved ^{14}C method described by Currie et al. (23) could be modified to eliminate this problem through an additional step of organic extraction of the ambient sample prior to ^{14}C analysis. This extraction step would all but

eliminate the interference due to adsorbed gases (CO_2) on the quartz filters because they would be lost during the evaporation of the solvent after the filter extraction. In addition, measurement of the the ^{14}C content of the major classes of condensable organics is now possible and could enhance the range of species used in receptor models. Another possibility for eliminating the artifact influence would be fractional distillation of the organics from the filter, followed by ^{14}C analysis of the individual thermally released organics. We would expect that only the fraction initially eluted from the filter would contain most of the artifactual ^{14}C.

Electron Microscopy: For many aerosol characterization programs elemental composition and/or ionic content is insufficient to determine the chemical and physical properties of ambient aerosols. Either transmission electron microscopy (TEM) or scanning electron microscopy (SEM) are in most cases the only tools to study the properties of individual fine particles. A combination of SEM and TEM x-ray analysis (EDX) of the elemental content of particles enhances the characterization. However, EDX cannot measure C, O, and N, and for certain types of particles, e.g., fly ash, elemental composition of the particle provides insufficient information to identify the particle. For this reason, size and shape coupled with elemental composition provides the information to deduce the morphology of the particles.

More complex techniques are often needed to identify particles; most are destructive techniques and include application of microchemical tests and hot-stage electron microscopy for the characterization of micrometer and sub-micrometer particles. Although these techniques have been used successfully with OM, only a few microscopists have extended these techniques to electron microscopes. Mamane (25), Mamane and de Pena (26), and Mamane and

Puschel (27) have described the application of these techniques to the analysis of a variety of ambient particle samples. The best examples of these microparticle reaction tests are the SEM/EDX analysis of $BaCl_2$-treated surfaces for sulfates (Figure 9) and nitron ($C_{20}H_{16}N_4$; 4, 5-dihydro-1, 4 diphenyl-3, 5 phenylimino-1, 2, 4-triazol)-treated surfaces for nitrates (Figure 10). The advantages of these techniques are as follows: a) the method detects ions that cannot be seen by EDX (e.g., nitrates); b) they are inexpensive, sensitive, specific and relatively rapid techniques to measure sulfates and nitrates; c) provide information on mixed individual particles, such as a mineral particle coated with a layer of nitrate or a fly ash particle coated with sulfate (Figure 9), that cannot be obtained by other conventional procedures.

With the hot-stage techniques, particles are exposed to a given temperature while being observed by TEM. During the heating decomposition, melting and sublimation take place. Although the information may not positively identify the particle, these methods can be confirmatory, eliminates certain possibilities and, with the use of other techniques, assists in the identification of the particles.

Collection of particles for electron microscopy is completely different from the collection for other bulk analytical techniques (as wet chemistry or XRF). The following are important when collecting the particles: a) collect into 3 to 4 size classes, b) particles should remain individual particles on the collection substrate; (this normally requires that short sampling time be used to collect the submicrometer particles and that long periods be used for the larger particles). Mamane et al. (27) describe the use of the Casella impactor to collect the appropriate samples for SEM and TEM analysis. Collection periods for submicrometer ambient particles is typically seconds

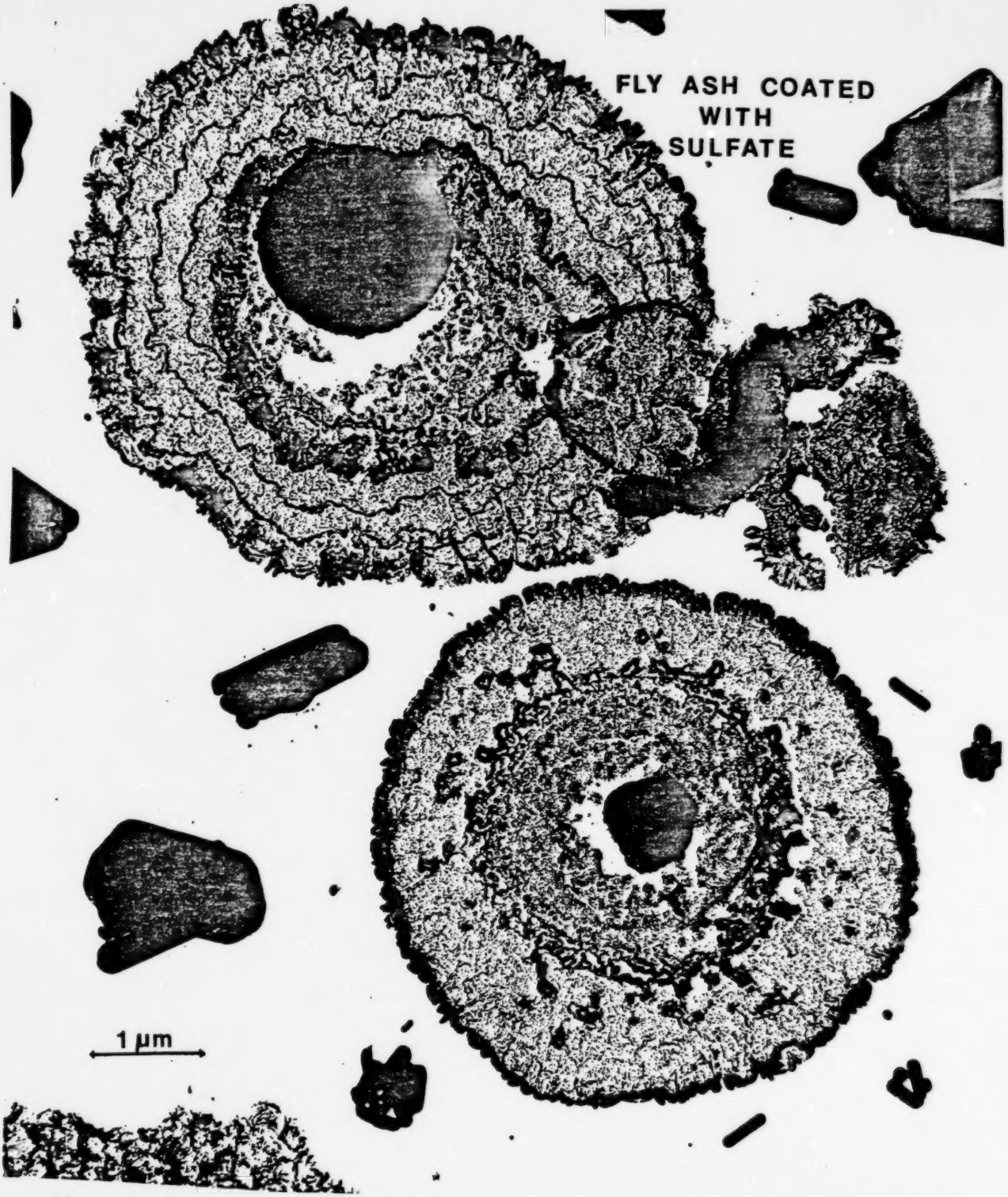


Figure 9. Reaction spot of sulfate particles with the $BaCl_2$ film, as viewed in the transmission electron microscope. Both sulfates contain insoluable nuclei, one of which is a fly ash particle. Sample was collected on Aug. 23, 1983, Deep Creek Lake, Maryland. Mixed sulfates were mostly found in evening and night samples, almost none during mid-day.

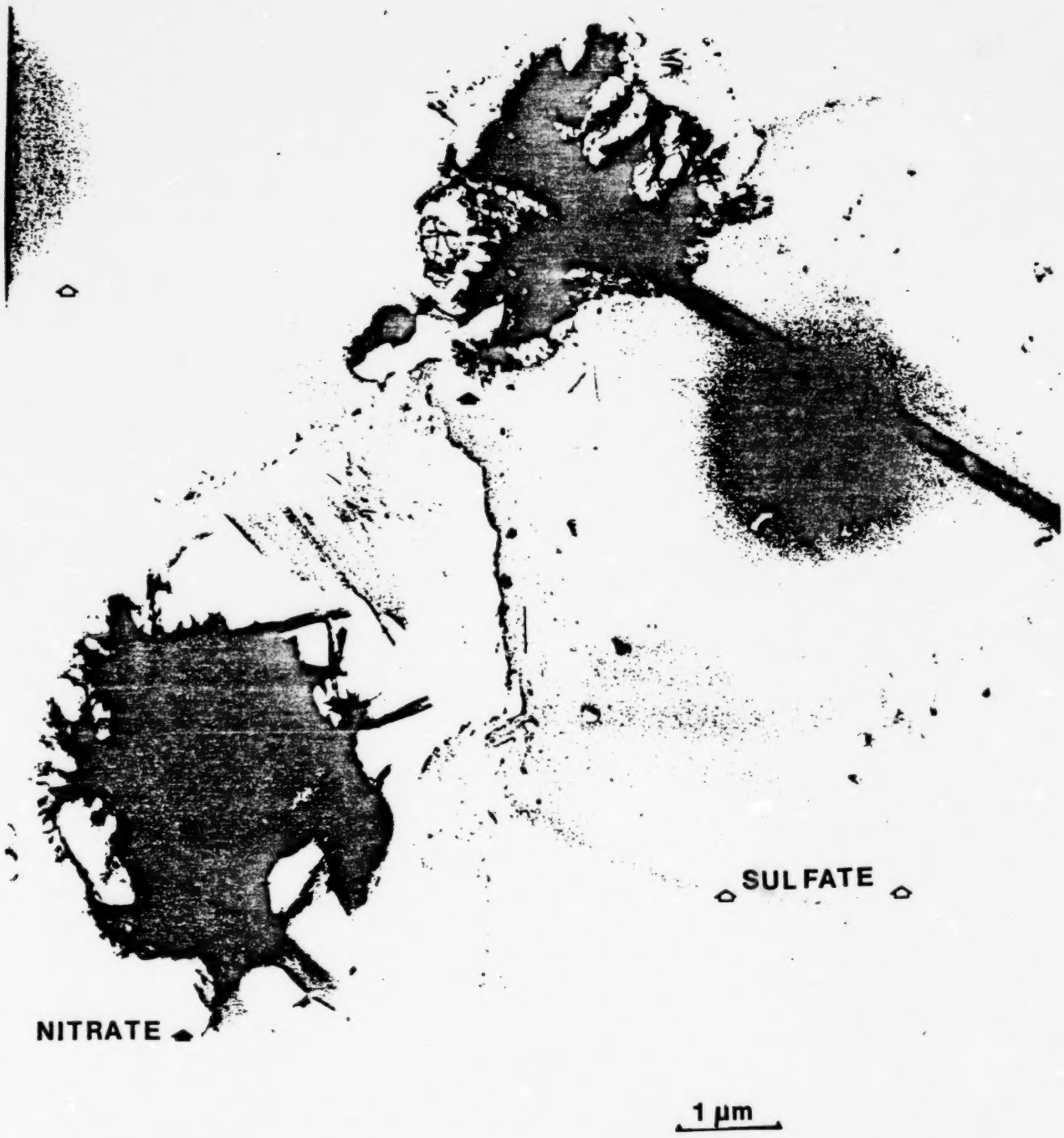


Figure 10. Reaction spots of nitrate and sulfate particles with nitron ($C_{20}H_{16}N_4$) film, as viewed in the transmission electron microscope. Sample was collected on Aug. 20, 1983, Deep Creek Lake, Maryland. Nitrates were found in particles larger than 1 µm and in very limited concentration.

and minutes for micrometer particles. Large particles (>10 μm) may need sampling times of a few hours. These sampling constraints tend to make comparisons between integrated measurements and SEM results difficult (29). However, these problems can be reduced through careful selection of sampling periods when bulk and particle-by-particle characterization are to be compared.

X-ray Diffraction and Optical Microscopy Much interest in the composition and source identification of atmospheric aerosols has developed over recent years. In most studies prior to the last decade, much of the compositional characteristics of particulates was inferred from wet chemical analyses, bulk-sample XRF analyses, and optical scattering characteristics. Some work with optical polarizing microscopy yielded results for the major components, but only for those particulates at the coarse end of the size distribution.

During the past decade much more effort has been expended toward development of techniques yielding direct compound identification. An example of a quantitative study of this type is found in the report of Bradway and Record (30) in which optical polarizing analysis of mineral particulates trapped on glass fiber (Hi-vol) filters is given for 14 urban areas. In the work of Stevens et al. (4), particulate compositions were deduced from ion equivalents required by stoichiometry of the compounds with ion chromatography, Thorin spectrophotometry, and x-ray fluorescence being employed as the analytical methods. Although not a direct observational technique, infrared absorption analysis does provide evidence of the presence of certain compounds according to the observed bond frequencies. Work of Adler and Kerr (31) and Moharram and Sowelim (32) provide infrared information on the occurrence of sulfate ions in various sulfate minerals. Some

particulate compounds may be identified by morphological characteristics and their composition deduced by single-particle microbeam scanning electron techniques that will be discussed later. Perhaps the most powerful tool for direct compound identification, both from a qualitative and a quantitative standpoint, is XRD. Difficulty in application of this technique to aerosols comes primarily from the low mass coverage of the particulates on the collecting filter media. Nevertheless, good qualitative studies reporting identification of atmospheric aerosols from filters have been completed by Biggins and Harrison (33), Thompson et al. (34), O'Connor and Jaklevic (35), and Brosset et al. (36). Several of these studies included a separation of the particulate mass into size fractions to identify the dominant compounds in each.

During the past five years, the Institute of Atmospheric Sciences' (IAS) Cloud Physics Laboratory at the South Dakota School of Mines, Rapid City, SD, has worked toward the development of a quantitative technique for analysis of particulate matter collected on various filter substrates. The results of these studies have been reported by Davis et al. (37) and Davis and Johnson (38 and 39). The basis for the technique is the reference intensity method combined with direct beam x-ray transmission measurements. These combined techniques allow the simultaneous determination of crystalline components and the major classes of amorphous components present in thin aerosol layers collected on filter substrates. Analyses may be completed using Teflon, glass fiber, cellulose acetate, quartz, and polycarbonate filter media.

The XRD procedure developed by Davis et al. (40) to measure the quartz content in ambient particles collected on Teflon filters is based on a mass calibration procedure. The basis of this calibration procedure rests on the provision that, for a monodisperse layer on a thin membrane filter, overlap is

negligible and matrix absorption can be ignored. For 3 μm radius spheres of 2.65 density (quartz), such particles can accumulate to the extent of 900 μg cm^{-2} before a monodisperse layer is formed on the filter. For these conditions, therefore, a given laboratory instrument under proper quality assurance procedures may maintain the target x-ray flux at a level sufficiently invariant to complete direct mass calibration analyses over an indefinite period of time. A Norelco diffractometer using a copper target raised to 40 kV and 20 mA power was used for these analyses. Samples were mounted on a Norelco high-angle goniometer fitted with a theta compensator, graphite crystal monochronometer, and spinning sample mount. All samples were scanned from 5° 2θ to 40° 2θ to make a semi-quantitative evaluation of other components. The ratio of peak height to reference intensity constant for each observed component provided a visual estimate of relative abundances for the semi-quantitative evaluation. The quartz peak at 26.67° 2θ (hkl = 101) was used as a basis for the quantitative calibration and analysis.

In conjunction with the reference intensity analysis program, a number of quartz samples were analyzed for scattering power (reference intensity constant values): the Tuscarora quartz was selected from this group as representative of quartz in the environment, the reference intensity constant being close to the average of the set of eight samples analyzed. A linear calibration curve was obtained between μg cm^{-2} and integrated intensity at the 26.67° quartz peak based on a total of 12 calibration analysis completed by loading Teflon filters with a specified weight of fine particulate Tuscarora quartz using an aerosol suspension technique described previously by Davis et al. (40). In the initial data set, the regression on the experimental points yielded a slope of 463 counts cm^2 μg^{-1} with an intercept of 5.1 μg cm^{-2}. The limit of detection for quartz was found to be 0.6 μg cm^{-2} for particles collected on Teflon filters.

These studies have included a formal "variance error" analysis based on uncertainties known to exist or anticipated in the various measurements and physical parameters. In general, weight quantities are known to within 10% for major components in the sample. For minor components (i.e., less than 10% of the total mass) errors are quite variable, but may be as high as 100% or greater in some cases.

Recently, Davis et al. (40) analyzed 104 pairs of Teflon filters collected in 1980 from 22 U.S. cities as part of the EPA's Inhalable Particulate Network (41). The filters were analyzed for elemental composition by EDXRF and for mineral content by an XRD procedure with the emphasis on the quartz content. Table 4A shows the elemental composition and quartz content of selected fine and coarse particles from four U.S. cities. Table 4B lists minerals that were observed to be present in almost all particle samples collected in the U.S. and their chemical composition.

From the analysis of these dichotomous filters from the 22 U.S. cities, it was noted that the continental interior sites showed the highest average ambient quartz concentration as well as the greatest variability. Coastal regions and eastern interior sites, with few exceptions, showed the lowest quartz concentrations in the ambient air. Perhaps the most notable exceptions to this generalization are the sites of Inglenook and Tarrant, located in industrialized north Birmingham, AL, and El Paso, TX, where a quartz level was observed that was lower than expected for an arid inland site.

Comparison of these data with analyses made with polarizing OM by Bradway and Record (30) shows some interesting relationships. The filters studied by Bradway and Record were obtained from standard Hi-vol samplers of the National Aerometric Sampling Network (NASN), which did not have a wind insensitive sampling inlet. Therefore, the concentrations of quartz observed from these

Table 4a. Elemental composition and quartz content of fine and coarse particles from three U.S. cities.

TYPICAL MASS-ELEMENTAL AND QUARTZ CONCENTRATION IN $\mu g/m^3$ AT SELECTED SITES IN THE UNITED STATES

	BOSTON, MASS		KANSAS CITY, MO		RIVERSIDE, CA	
	FINE	COARSE	FINE	COARSE	FINE	COARSE
MASS	34.9	105.9	25.7	44.7	35.2	71.0
AL	-	3.458	.091	2.053	0.036	3.513
SI	0.144	6.760	.434	4.542	.234	7.544
S	3.869	.502	1.816	.215	1.653	.720
Cl	-	.301	-	-	.009	.164
K	.096	.533	.311	.349	.120	.961
Ca	.070	1.069	.519	3.852	.301	4.781
V	.020	.008	-	-	.003	-
Fe	.121	1.612	.189	.800	.127	1.888
Ni	.012	.022	.002	.003	.007	.006
Cu	.035	.023	.032	.016	.040	.021
Zn	.046	.054	.034	.026	.029	.030
Br	.020	.025	.027	.009	.037	.028
Pb	.285	.177	.180	.057	.376	.113
QUARTZ	0	8.00	0	4.70	0	3.00

Table 4b. Minerals commonly found in ambient particles.

MINERALS COMMONLY PRESENT IN AMBIENT PARTICLES THAT CAN BE MEASURED BY X-RAY DIFFRACTION METHODOLOGY

MINERAL NAME	COMPOSITION
BIOTITE	$K_2MgFe_3(FeAl)Al_3Si_3)O_2 \cdot (OH)_3$
MUSCOVITE	$KAl_2(AlSi_3O_{10})(OH)_2$
GYPSUM	$CASO_4 \cdot 2H_2O$
KALONITE	$(Fe,al)_4\ Si_4O_{10}(OH)_8$
CALCITE	$CaCO_3$
PLAGIOCLASE	$0.55\ [NaAlSi_3O_8] + 0.45\ \ [CaAl_2Si_2O_8]$
DOLOMITE	$CaMg(CO_3)_2$
HEMATITE	Fe_2O_3
MAGNETITE	$FeO \cdot F_2O_3$
ANGLESITE	$PBSO_4$
MASCAGNITE	$[NH_4]_2SO_4$
THENARDITE	Na_2SO_4
SODANITER	$Na\ NO_3$
CHLORITE	NaCl

analyses should be considerably higher, in terms of weight percent of total suspended particulate (TSP), than those values obtained from the dichotomous sampler. Such is actually observed by comparison of the Bradway and Record (30) data with those of this paper. Three cities that were common to both the Bradway and Record (30) OM and the Davis et al. (40) XRD, OM particle classification studies were: North Birmingham, (Tarrand and Inglenook), St. Louis, MO, and Cincinnati, OH. In the Birmingham study, the Bradway and Record analyses showed 21 weight per cent quartz as an average of six filters, with the aerodynamic diameter particle size ranging from 5 to 60 μm with a median of about 15-μm diameter. This high level may be contrasted to the 4-7% observed in the dichotomous coarse fraction. Similarly, high values were observed by Bradway and Record in St. Louis (26 weight per cent for the 26-filter average, 6 sites). The presence of 40% calcite in the optical study agrees with our observation by XRD that calcite and dolomite constitute a significant fraction of the St. Louis filter mass. A similar result was obtained at Cincinnati where 19% quartz and 22% calcite was observed optically for the 20-filter average.

Quartz is often a major source of silicon in the coarse particle fraction of ambient aerosols. Feldspars, micas, and clays, however, contribute significant amounts of silicon in certain localities.

Davis' et al. (40) examination of the relationship between the silicon and quartz concentration for Buffalo, NY indicates that quartz was the major contributor of silicon, whereas less of a relative contribution from quartz was found in the samples from Birmingham and only very little was found from the Portland, OR site. Indeed, the examination of the XRD charts revealed that feldspars were the primary crustal component of the aerosols at Portland, OR, whereas at Buffalo only an occasional occurrence of feldspars and micas

were observed; the other constituents were primarily carbonates and sulfates. This feature is also consistent with the higher Al and K contents of the Portland, OR sample.

DENUDER SAMPLERS

Nitrate and Nitric Acid Measurements: Evidence is accumulating that indicates the importance of acidic nitrate in atmosphere deposition processes. For example, Lewis and Grant (42) have recently reported measurements of precipitation chemistry from a rural site in the Colorado Rockies and suggest that a decrease of nearly one pH unit over a period of four years was due to increasing nitric acid. The nature of nitrate deposition depends on the distribution of nitrates between gas and solid phases. A number of investigators (43) and (44) have recently made observations that indicate that, in both rural and urban atmospheres, gaseous nitrate concentrations are considerably larger than those of particulate nitrate. The contrasting behavior of atmospheric nitric acid (HNO_3), which appears in the gas phase, and sulfuric acid (H_2SO_4), which appears in particulate form, is consistent with their relative vapor pressures and heats of hydration.

The determination of background or rural values for nitrates is difficult; even at 10,000 ft in the Rocky Mountains, Kelley et al. (45) have observed changes in HNO_3 concentrations of a factor of 100 depending on whether the wind was from the east or west. It is clear that techniques for measuring atmospheric nitrates should combine high sensitivity with unambiguous discrimination between gaseous and particulate nitrates.

As investigators have improved methods of sampling and analysis for atmospheric nitrate, it has become evident that the distribution of atmospheric nitrate between the gaseous and particulate phases has been masked

by experimental artifacts. Many early particulate nitrate data were based on analyses of extracts from glass fiber aerosol filters used in Hi-vol samplers. It is now known that these filters contain active sites that fix gaseous HNO_3 and make it appear as particulate nitrate (46, 47). Other filter materials have also been shown to react with and collect gaseous HNO_3 and create a positive particulate nitrate artifact (48). The use of an inert filter material such as Teflon removes the "positive artifact" problem, except for the possibility of reaction with the collected aerosol particles. It has been shown, however, that collected aerosol nitrate particles (true particulate nitrate) may be lost from filters due to reactions with other materials or to evaporation. Loss of particulate nitrate is known as "negative artifact." Reactive loss may occur if, for example, H_2SO_4 aerosol comes in contact on the filter surface with nitrate aerosol. Evaporative loss may occur due to decreases in ambient gas concentrations causing the solid and gaseous nitrate phases to no longer be in equilibrium. Thus we see that, on the one hand, measurements of particulate nitrate using glass fiber filters are expected to be systematically high. If the recent measurements mentioned above of the distribution between HNO_3 and particulate nitrate are correct, the glass fiber filter nitrate overestimates may be considerable. On the other hand, measurements of particulate nitrate using inert Teflon filters are expected to be systematically low, but the extent of loss due to reaction and evaporation are difficult to predict.

Given the free energy change of vaporization for NH_4NO_3, it is straightforward to calculate the vapor pressures of NH_3 and HNO_3 in equilibrium with NH_4NO_3 in the solid phase (49). These calculations show that at 10°C and 30°C the gas-phase equilibrium concentrations of both NH_3 and HNO_3 required to sustain the solid phase are $\cong$4 and 12 ppb, respectively.

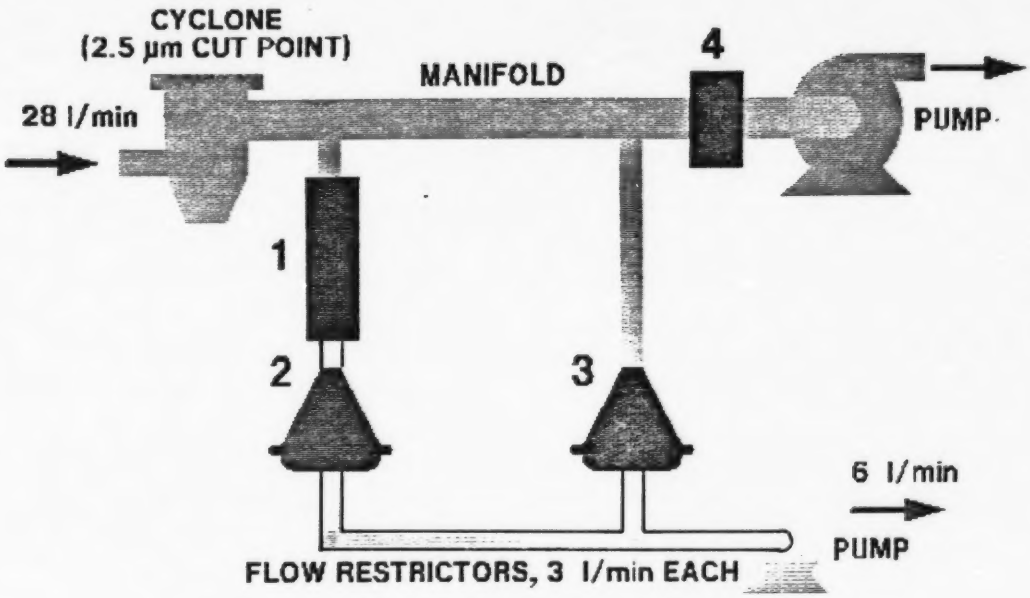
Tang (50) carried out considerably more detailed studies of the vapor pressures of HNO_3 and NH_3 in equilibrium with solution droplets of ammonium salts and has estimated the dependence of these vapor pressures on humidity and droplet acidity. Tang's work provides quantitative estimates of the increase of HNO_3 and decrease of NH_3 vapor pressures with increasing acidity and of the decrease of HNO_3 and NH_3 vapor pressures with increasing humidity.

Given the results of these calculations for estimating gas phase concentrations of NH_3 and HNO_3 required to support solid or solution phase nitrate and given the typical observed values of ambient NH_3 and HNO_3 concentrations, one may wonder why nitrates are ever observed in particles except in extraordinary circumstances. The components of the atmosphere, however, are generally not at thermodynamic equilibrium and the rate of approach to equilibrium between the solid and gas phase may be decreased by the intervention of other materials or phases. For example, the vapor pressure of water above a saturated solution of NH_4NO_3 is such that the solid phase is hygroscopic at relative humidites >60% over the temperature range 20-30°C. This means that at relative humidities exceeding 60%, particles of NH_4NO_3 will accumulate an aqueous layer. As long as the solid phase is present, the equilibrium vapor pressures of NH_3 and HNO_3 will be unchanged, but the rate of approach to equilibrium will be retarded. Alternatively, a particle may accumulate a layer of atmospheric organic material that would retard the loss of material from the solid to the gas phase. Because the nonpolar organic molecules will reduce the dielectric constant of the solution, it is energetically favorable for them to remain on the surface of the particle; hence, a skin may be formed. Chang and Hill (51) have shown that aqueous drop evaporation is retarded by the accumulation of gaseous mixtures of ozone and olefins and they provide references to earlier work on

the reduction of evaporation by organic films. Apparently, losses of atmospheric particles due to evaporation are strongly dependent on other components in the atmosphere. It may be for these reasons that nitrate in aerosols is stabilized with respect to evaporation.

Denuder Difference Method: In order to avoid both positive and negative nitrate artifacts, a sampling system developed by Shaw et al. (52) has been tested and has been used in a number of EPA field studies. The system, termed the denuder difference method (DDM), is shown in Figure 11a. Figure 11b is a photograph of a combined DDM and fine particle collection device to measure sulfate, fine particle mass, and SO_2. The experimental set-up for the DDM consists of Teflon cyclone to remove the coarse particles. The ambient air passes through the cyclone at ~ 30 L/min, and into a manifold where two parallel samples are collected at 3 L/min downstream of two tubes. One of the tubes, the denuder, is coated with MgO; the other tube, constructed of Teflon, is uncoated. The residence time of the gas and fine particles in the denuder is 0.2 s. After the air sample exits the tubes, it passes through a 25-mm diameter, 1-μm pore size Membrana nylon filter. The MgO removes the HNO_3 and the true fine particle nitrate is collected on the nylon filter. On the other nylon filter HNO_3 + fine particle nitrate is collected. The difference between the HNO_3 + nitrate sample and the fine nitrate is HNO_3, hence the name of the method.

The nylon filters are removed and stored in a sealed dessicator at 5°C until they are extracted. The nylon filters are extracted in 1×10^{-5} $NaHCO_3$ solution in an ultrasonic bath. The extract is analyzed by ion exchange chromatography for nitrate content. The precision of the method for 19 replicates is: nitrate = 0.1 μg/m³, nitric acid = 0.2 μg/m³. The precision refers to an ambient air sample size of 2.0 m³. Figure 12 is a bar graph that



1. DENUDER, MgO COATED (REMOVES HNO_3)
2. FILTER, NYLON (COLLECTS NITRATE AEROSOLS)
3. FILTER, NYLON (COLLECTS HNO_3, NITRATES, AEROSOLS)
4. DIFFERENTIAL FLOW CONTROLLER

Figure 11a. Denuder difference method (DDM) sampler.

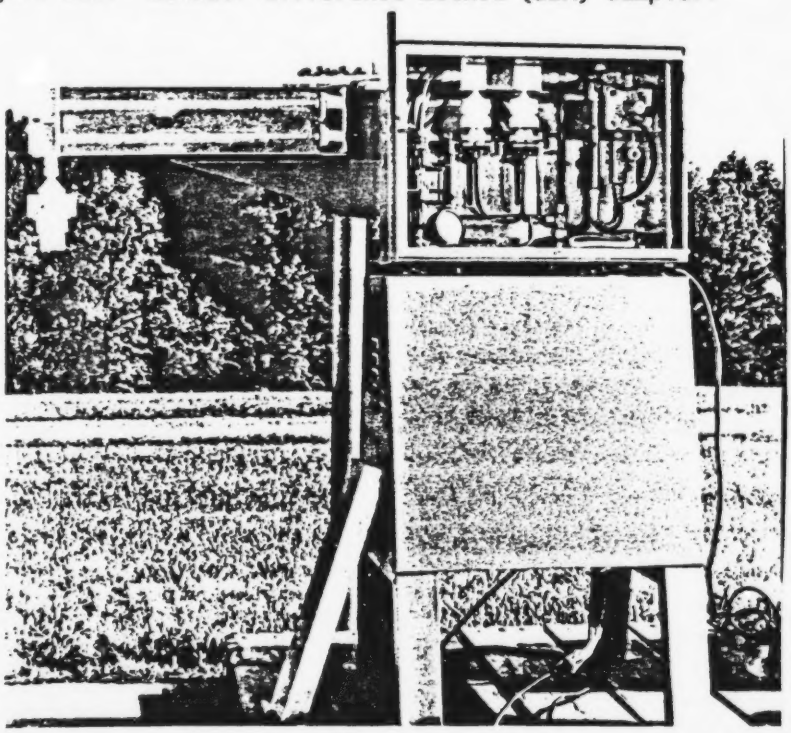


Figure 11b. Photograph of DDM samples and fine particle collector.

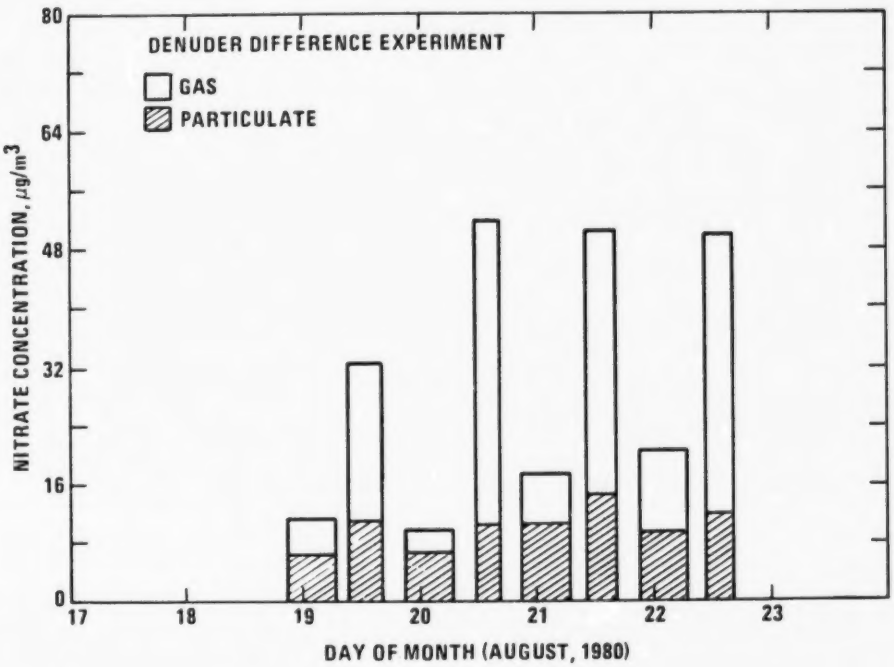


Figure 12. Bar graph of denuder difference results for samples collected in N.C., 1982.

compares measurements of gaseous nitrate and particle nitrate obtained using the DDM during the summer of 1980 in Research Triangle Park, NC.

Annular Denuders: During the past two years a new design for denuders has been developed and tested at the Laboratory for Atmospheric Pollution of C.N.R., Rome, (Italy), which has led to a device described by Possanzini et al. (54) that is suitable for the simultaneous measurement of different species contributing to deposition.

The C.N.R. denuder is an annular tube configuration (Fig. 13). During sampling, air is drawn under laminar flow conditions through the annular space between two concentric glass cylinders that have been coated with a chemical that reacts with selected trace species. As the sample stream passes through the annular space, the gaseous trace species travel by molecular diffusion from the bulk gas to the reactive surface and are collected.

The reader is referred to the work of Pozzanini, et al. (54) for a discussion of annular denuder tube theory. A description of the ADM design characteristics and operating parameters used to collect ambient samples is shown in Table 5.

For a given flow the annular denuder method (ADM) can achieve equivalent collection efficiency in ~1/30 of the length required for an open-tube denuder, or for a given denuder length, the annular denuder can sample at ~ 30 times the flow of an open-tube denuder.

The high operating flow rate (10-30 ℓmin^{-1}) makes the annular denuder very useful for experiments where collection of low concentration of certain gases are required over short term sampling (1-4 h) periods. The high flow rate also permits more material to be collected on membrane filters downstream of the denuder. Previously, collection of large quantities of particles while simultaneously preserving the integrity of the particles through removal of

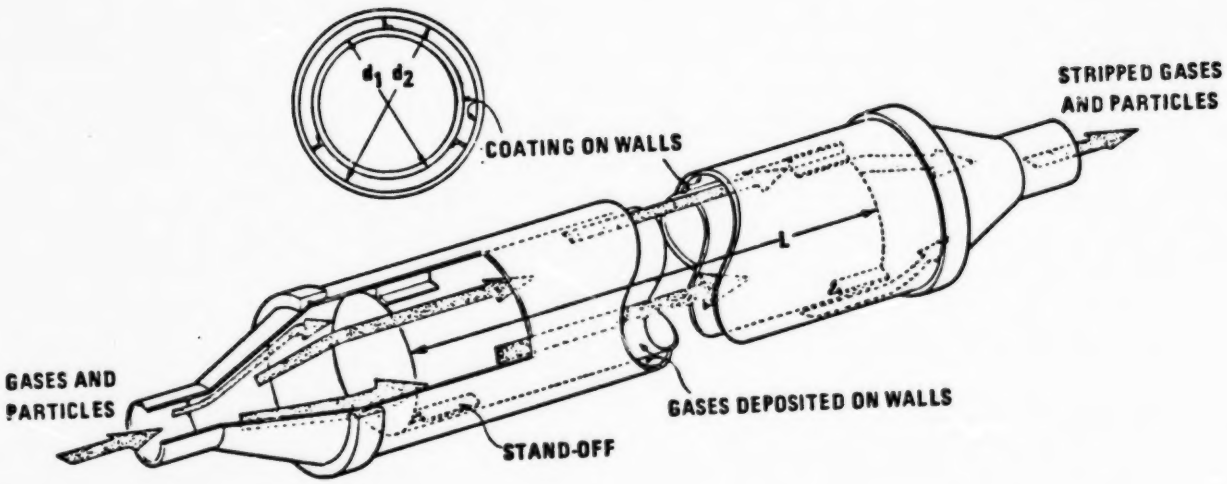


Figure 13. Annular denuder

reactive gases (eg, HNO_3, NH_3, and SO_2) required that the filter be preceded by a parallel multitube denuder assembly similar to that described by Stevens, et al. (4).

For a denuder to be effective, the system needs to ensure separation of the gases and particles. However, diffusional and inertial deposition at the inlet can result in particle uptake which has been determined experimentally (Possanzini et al., 54) to be not larger than about 3%. The transit time of air through the denuder is <0.1 second, reducing the opportunity for substantial disturbance of the atmospheric gas-particle equilibrium existing in the atmosphere. The walls of the denuder are etched by sand blasting with 100 μm sand particles. This feature increases the surface area available for chemical coating, and, as a result, the capacity of the denuder to collect the pollutants of interest can be increased to several milligrams. A diagram of the annular denuder system which was evaluated by the EPA in Research Triangle Park, NC is shown in Figure 14.

The use of a water soluble and IC compatible substrate to coat the walls of the annular tube (e.g., Na_2CO_3) shown in Fig. 14 simplifies the extraction and the analysis of the sample. Other substances deposited on the denuder may give rise to the formation of the same ions; for example, deposition of particulate matter containing chlorides, sulfates, and nitrates interfere with the measurement of HCl, SO_2 and HNO_3. The absorption of NO_2 and PAN on Na_2CO_3 yield nitrites which interfere with the measurement of HNO_2. However, the efficiency for the collection of these interfering species is relatively small (about 1 to 3%) (Ferm and Sjödin, 55). Therefore, the ADM uses two annular denuders connected in series as shown in Figure 14 in field studies where SO_2, HNO_3, nitrate sulfates and related species are to be measured. Thus, in this configuration the amount of relatively unreactive interferents collected in

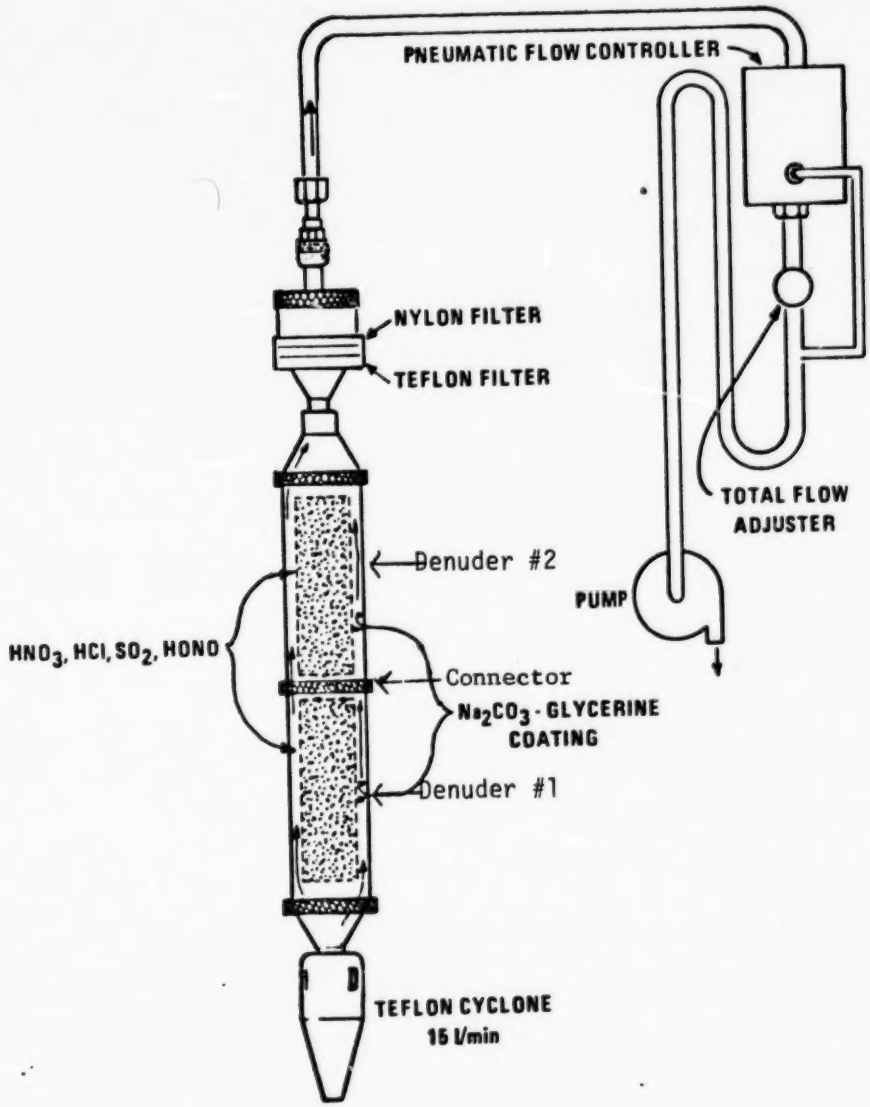


Figure 14. Annular denuder: a filter pack system used to collect HNO_3, HCl, SO_2, NO_3^-, HONO, $SO_4^=$, and H^+.

the first denuder will be approximately equal to that found in the second denuder. This feature can be used to correct data obtained from the analysis of the first denuder. The use of two denuders in series will then permit the simultaneous analysis of several acidic compounds, even though the ratio of analytes in the gas phase and particulate matter is extremely low. For instance, the technique would be is valuable for the measurement of trace levels (< 0.1 $\mu g/m^3$) of SO_2 and HNO_3 in the presence of large quantities of sulfates and nitrates in particulate matter, and, in addition, the use of two denuders will permit the measurement of small amounts of HNO_2.

A typical chromatogram obtained from IC analysis of annular denuder extracts is shown in Fig. 15. There is no visual evidence of $SO_4^=$ or NO_3^- in the second denuder; this shows the high collection efficiency of the first denuder for HNO_3 and SO_2 and implies that deposition of particles in the denuder is low. Absence of NO_2^- in the second denuder is interpreted as an indication that the NO_2^- in the first denuder is due to a very reactive species such as HNO_2 rather than PAN or NO_2, which react much more slowly with the Na_2CO_3 denuder surface (Ferm and Sjödin, 55).

A sample collection system based on annular denuders followed by particulate filters appears to be a very promising system for measurement of HNO_3, NO_3^-, SO_2, $SO_4^=$, NH_3, NH_4^+ and H^+. The system's main features are: (a) operation at a relatively high flow rate while maintaining a collection efficiency greater than 95%; (b) use of denuder coatings which are extractable in water and compatible with conventional IC analysis; (c) single flow train and corresponding reduction in the number (and cost) of flow control devices; (d) relatively easy to set up and operate; (e) all gases of interest are removed from the sample stream by denuders prior to passage of the sample stream through any filter medium. In this configuration the acidification or

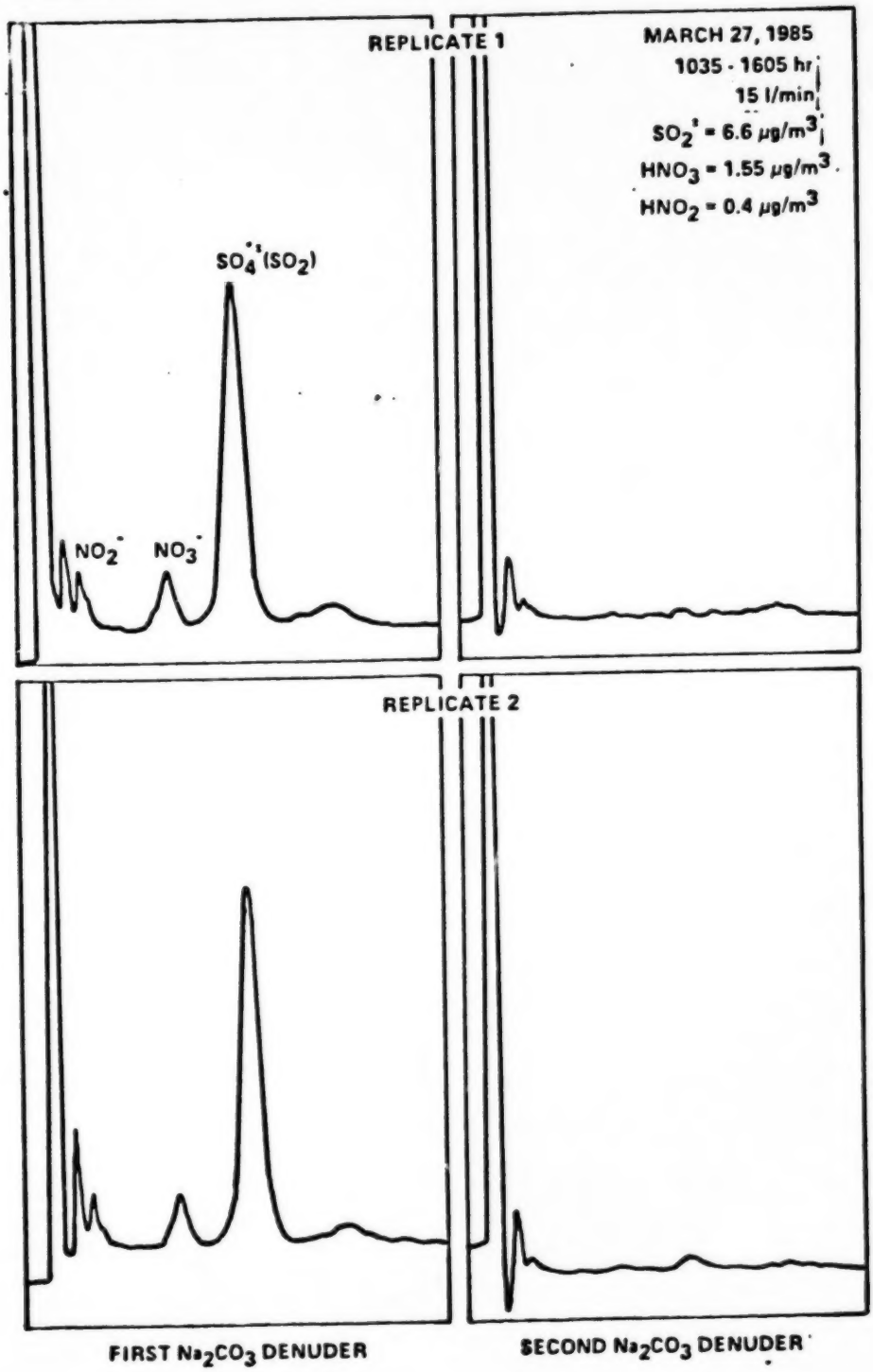


Figure 15. Typical ion chromatogram of parallel annular denuders which have collected ambient air samples. The second denuder after the first denuder does not contain measurable amounts of $SO_4^{=}$ or NO_3^- indicating the efficiency of the first denuder.

neutralization of particles on filters is minimized. The configuration of an annular denuder assembly: filter pack system built and being tested by the CNR Research Group in Italy to measure the aforementioned species is shown in Fig. 16.

Table 5. Characteristics of an Annular Denuder System.

	ADM
Denuder:	381 x 38 mm
Annular Space:	1.5 mm
Coating:	Na_2CO_3: glycerine
Flow Rate:	15 LPM
Filters:	47 mm 2 μm Teflon
	47 mm 1 μm Nylon
Species Measured:	HNO_3, SO_2, NO_3^-, $SO_4^=$
	NH_3, (HNO_2), (H^+)
Analysis:	IC, Colorimetry

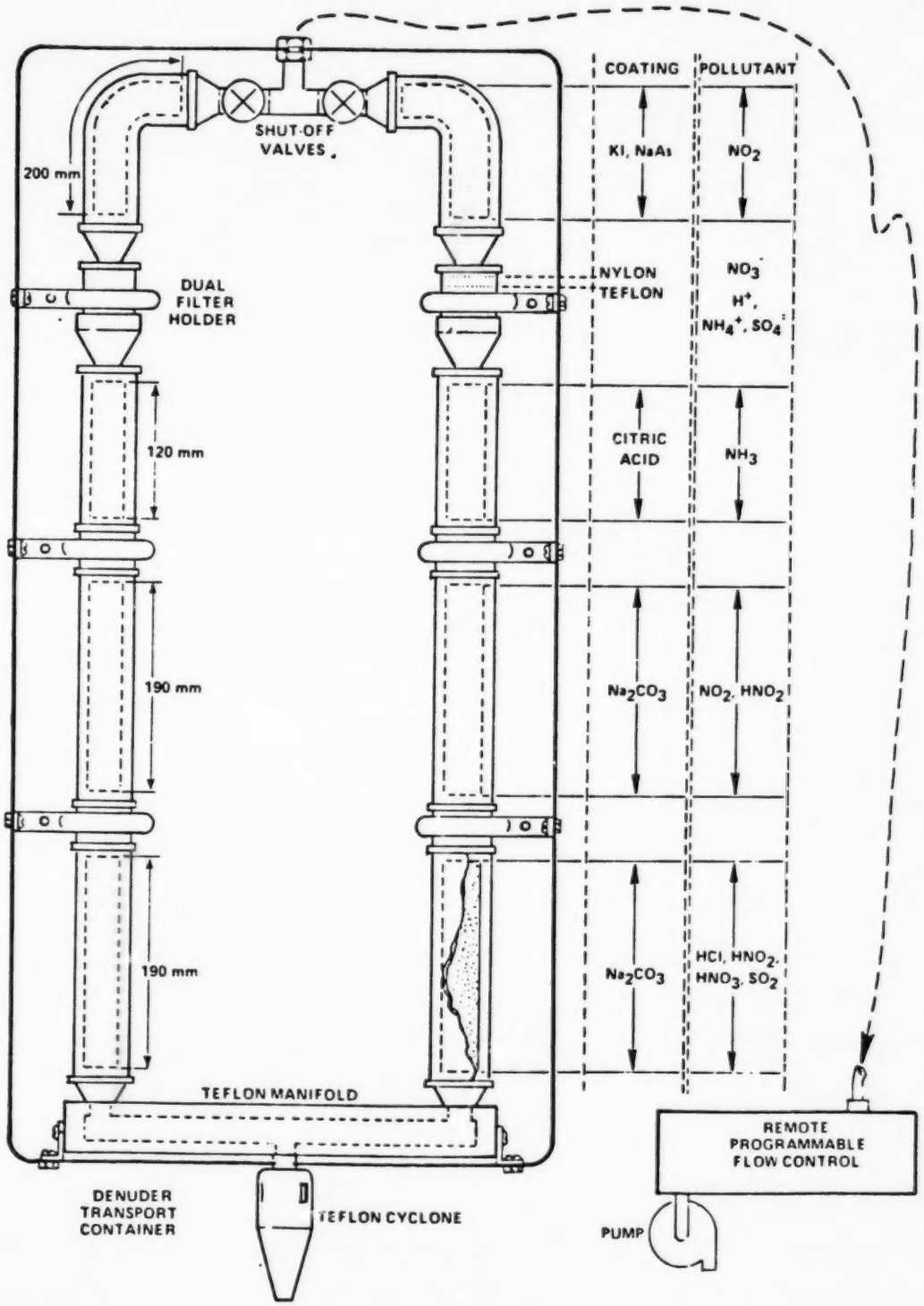


Figure 16. US-Italy annular denuder acid deposition sampling system.

Conclusions

The major conclusions that can be drawn from this review of sampling and analytical methods to measure the composition of ambient particulate samples are as follows:

1. Collection of aerosols into two size ranges, fine and coarse fractions, simplifies the chemical analysis and preserves chemical integrity of acid species present in fine particles by removing the alkaline coarse particles before the particles are deposited onto the appropriate filter.

2. Two-micron pore size Teflon filters are recommended for particle collection when mass, elemental and ionic composition, and x-ray diffraction properties of the particles are to be measured.

3. Energy dispersive X-ray Fluorescence (XRF) Analysis and Neutron Activation Analysis are ideal analytical methods to measure the elemental composition of most of the elements present in ambient particles. XRF methods are preferred, because the analysis is completely non-destructive, highly sensitive, and can measure to within ± 10% such elements as Pb, Br, Cl, S, Cu, Si, Fe, Cu, K, As, Se and Cd at levels typically found in urban atmospheres.

4. Quartz filters are recommended when the carbon content of the particulate matter is to be measured. Combustion of the particulate samples at 650°C and 850°C differentiates the elemental or soot carbon from condensable organics present in ambient aerosols.

5. Sampling aerosols for microscopic or scanning electron microscopic analysis requires much shorter collection periods than for bulk elemental composition measurements.

6. Aerosol nitrate and nitric acid can only be reliably measured by use of HNO_3 denuders and nylon (or equivalent) filter materials.

7. Ion exchange chromatographic methods are recommended for the measurement of most anions and cations present in ambient particulate samples. If the appropriate precautions are followed, sulfites that may be if present in ambient particles can also be measured by ion chromatographic procedures.

8. X-ray diffraction can measure mineral content of particulate if the mass of particles per unit area on the filter is $\geq$ 200 μg/cm and soil standards from the airshed are available.

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Disclaimer:

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References

1. Stevens R.K. and Pace T. (1984) Overview of mathematical and empirical receptor models workshop. Atmospheric Environment. In press.

2. Stevens R.K. (1979) Current methods to measure atmospheric nitric acid and nitrate artifacts. Report EPA-600/2-79-051, U.S. Environmental Protection Agency, Research Triangle Park, NC.

3. Liu B., Pui D., Rubow K. and Kuhley G. (1978) Research on air sampling filter media. Progress Report -- Grant Report R804600, Univ. of MN, Minneapolis, MN.

4. Stevens R. K., Dzubay T. G., Russwurm G. M. and Rickel D. (1978) Sampling and analysis of atmospheric sulfate and related species. Atmospheric Environment 12, 55-68.

5. Huntzicker J.J., Johnson R. L., Shah J. J. and Coy R. A. (1982) An evolution of organic and elemental carbon in ambient aerosols by a thermal-optical method. In Atmospheric Life Cycle 77-78 (Edited by Wolff, G.T. and Klimisch, R. L.) Plenum Press, New York.

6. John W. and Reischl Georg (1980) A cyclone for size-selective sampling of ambient air. J. Air Poll. Control Assoc. 30, 872-876.

7. Lippmann M. and Chan T. Cyclone sampler performance. (1979) Staub Reinhart. Luft 39: 7-11.

8. Jaklevic J. M., Gatti R. C., Goulding F. S and Loo B. W. (1981) A β-gauge method applied to aerosol samples. Envir. Sci. Technol. 15, 680-686.

9. Courtney W. J., Shaw R.W., Jr. and Dzubay T. G. (1982) Precision and accuracy of a β-gauge for aerosol mass determination. Envir. Sci. Technol. 16, 236-239.

10. Scott D. R., Loseke W. A., Holbroke L. E. and Thompson R. J. (1976) Appl. Spectrosc., 30 (4) 392.

11. Jaklevic J. M., Landis D. A. and Goulding F. S. (1976) Energy dispersive x-ray fluorescence spectrometry using pulsed x-ray excitation. Adv in X-ray Anal. 19, 253-265, Kendall/Hunt, Dubuque, IO.

12. Currie L.A. (1977) Detection and quantitation in x-ray fluorescence spectrometry. In X-ray Fluorescence Analysis of Environmental Samples, pp. 289-306, Ann Arbor, Ann Arbor, MI.

13. Jaklevic J.M., Goulding F.S., Jarrett B.V. and Meng, J.D. (1974) Application of x-ray fluorescence techniques to measure elemental composition of particles in the atmosphere. Analytical Methods Applied to Air Pollution Measurements (Edited by Stevens, R.K.), pp. 123-146, Ann Arbor, Ann Arbor, MI.

14. Kowalczyk G.S., Gordon G.E. and Rheingrover S.W. (1982) Identification of atmospheric particulate sources in Washington, DC using chemical element balances. Envir. Sci. Technol. 16, 79-83.

15. Gordon G.E., Rheingrover S.W. and Aras N.K. (1982) Determining compositions of particles from major sources from ambient samples. Trans. Am. Nucl. Soc. 41, 199-.

16. Watson J.G. (1979) Chemical element balance receptor model methodology for assessing the sources of fine and total suspended particulate matter in Portland, OR. Ph.D. dissertation, Oregon Graduate Center, Beaverton, OR.

17. Core J.E., Hanrahan P.L., and Cooper J.A. (1981) Air particulate control strategy development: a new approach using chemical mass balance methods. In Atmos. Aerosol.: Source/Air Quality Relationships (Edited by Macias and Hopke) ACS Sym. Series No. 167, American Chemical Society, Washington, DC.

18. Brosset C. and Ferm M. (1976) Man-made airborne acidity and its determination. IVL Publications B-34B, Gothenburg, Sweden.

19. Mulik J., Puckett R., Williams D. and Sawicki E., (1976) Ion chromatographic analysis of sulfate and nitrate in ambient aerosol. Analyt. Lett. 9, 653-663.

20. Abbas, R. and Tanner, R. (1981) Continuous Determination of Gaseous ammonia in the ambient atmosphere using fluorescence derivatization. Atmospheric Environment 15, 277-281.

21. Stevens R.K., McClenny W.A., Dzubay T.G., Mason M.A. and Courtney W.J. (1982) Analytical methods to measure carbonaceous content of aerosols. In Atmospheric Life Cycle, (Edited by Wolff, G.T. and Klimisch, R.L.), pp. 111-129, Plenum Press, New York.

22. Cadle S.H., Groblicki P.J. and Mulawa P.A. (1981) Problems in the sampling and analysis of carbon particulate. General Motors Research Publication, GMR-3935, ENV #19; available from GM Research Laboratories, Warren, MI 48090.

23. Currie L.A. (1982) Contemporary particulate carbon. In Particulate Carbon, Atmospheric Life Cycle (edited by Wolff G.T. and Klimisch R.L.), pp. 245-260, Plenum Press, New York.

23. Currie L.A., Klouda G.A., Continetti R.E., Kaplan I.R., Wong W.W., Dzubay T.G. and Stevens R.K. (1983) On the origin of carbonaceous particles in American cities: results of radiocarbon 'dating' and chemical characterization. Proc. 11th Int. Radiocarbon Conference, Vol. 25, (edited by Stuiver, M. and Kra, R.).

25. Stevens R.K., Dzubay T.G., Lewis C.W. and Shaw R.W., Jr. (1984) Source apportionment methods applied to the determination of the origin of ambient aerosols that affect visibility in forested areas. Atmospheric Environment 18, 261.

26. Mamane Y. (1977) A quantitative method for the detection of individual submicron sulfate particles. Ph.D. thesis, 142 pp. Pennsylvania State University, University Park, PA 16802.

27. Mamane Y. and de Pena R. (1978) A quantitative method for the detection of individual submicrometer size sulfate particles. Atmospheric Environment 12, 69-82.

28. Mamane Y. and Pueschel R.F. (1980) A method for the detection of individual nitrate particles. Atmospheric Environment 14, 629-639.

29. Mamane Y. and Noll K. (1984) The use of micro-spot techniques to provide evidence of heterogeneous sulfur oxide and nitrogen oxide chemistry. Presented at National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources, Raleigh, NC

30. Bradway R. M., Record F. A. and Pace T. G. (1976) Application of polarizing microscopy to the characterization of ambient suspended particulate. Proceed. Ann. Meet. Fed. Analy. Chem. Spectros. Soc. Phila, PA Standard Oil Co., Cleveland, OH.

31. Bradway R.M. and Record F.A. (1976) National assessment of the urban particulate problem II: particle characterization Report EPA-450; 3-76-025, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency.

32. Adler H.H. and Kerr P.F. (1965) Variations in infrared spectra, molecular symmetry, and site symmetry of sulfate minerals. Am. Min. 50, 132-147.

33. Moharram M.A. and Sowelim M.A. (1980) Infrared study of minerals and compounds in atmospheric dust fall in Cairo. Atmospheric Environment 14, 853-856.

34. Biggins P.D.E. and Harrison R.M. (1979) Atmospheric chemistry of automotive lead. Envir. Sci. Technol. 13, 558-565.

35. Thompson A.C., Jaklevic J.M., O'Connor B.H. and Morris C.M. (1982) X-ray powder diffraction system for chemical speciation of particulate aerosol samples. Nuclear Instruments and Methods, 198, 539-546.

36. O'Connor B.H. and Jaklevic J.M. (1980) X-ray diffractometry of airborne particulates deposited on membrane filters. X-ray Spectrometry 9, 60-65.

37. Brosset C., Andreasson K., and Ferm M. (1975) The nature and possible origin of acid particles observed at the Swedish west coast. Atmospheric Environment 9, 631-642.

38. Davis B.L., Johnson L.R., Stevens R.K., Gatz D.F. and Stensland G.J. (1982) Observations of sulfate compounds of filter substrates by means of X-ray diffraction. In Am. Geoph. Union Monogr. 26, 149-156.

39. Davis B.L. and Johnson L.R. (1982) Sample preparation and methodology for x-ray quantitative analysis of thin aerosol layers deposited on glass fiber and membrane filters. Adv. in X-ray Analysis 25, 295-300.

40. Davis B.L. and Johnson L.R. (1979) X-ray diffraction analysis in aerosol provenance studies. Preprints of the 72nd Annual Meeting, A.I.Ch.E., San Francisco, paper 118c.

41. Davis B.L., Johnson R.L., Stevens R.K., Courtney W.J. and Safriet D.W. (1984) The quartz content and elemental composition of aerosols from selected sites of the EPA inhalable particulate network. Atmospheric Environment 18, In press.

42. Suggs J.C., Rodes C.E., Evans E.G. and Baumgardner R.E. (1981) Inhalable particulate network annual report; operation and data summary (mass concentration only). April 1979-June 1980, EPA-600-4-81-037 (available from NTIS, Springfield, VA 22161]).

43. Lewis W.M. and Grant M.C. (1980) Acid precipitation in the Western United States. Science 207, 176-177.

44. Huebert B.J. and Lazrus A.L. (1980) Tropospheric gas-phase and particulate nitrate measurements. J. Geophys. Res. Section C85, No. C-12, 7322-7328.

45. Spicer C.W. (1977) Photochemical atmospheric pollutants derived from nitrogen oxides. Atmospheric Environment 11, 1089-1095.

46. Kelly T.J., Steadman, D.H., Ritter, J.A. and Harvey R.B. (1980) Measurements of oxides of nitrogen and nitric acid in clean air. J. Geophys. Res. Section C, 85, No. C, 7117-7125.

47. Pierson W.R., Butler J.W. and Trayser D.A. (1974) Nitrate and nitric acid emission from catalyst equipped automotive systems. Envir Lett. 7, 267-273.

48. Appel B.R., Tokiwa Y. and Haik M. (1980) Sampling of nitrates in ambient air. Atmospheric Environment 15, 283-289.

49. Spicer C.W. and Schumacher P.M. (1977) Interferences in sampling atmospheric particulate nitrate. Atmospheric Environment 11, 873-876.

50. Stelson A.W., Friedlander S.K. and Seinfeld J.H. (1979) A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate. Atmospheric Environment 13, 369-371.

51. Tang I.N. (1980) On the equilibrium partial pressure of nitric acid and ammonia in the atmosphere. Atmospheric Environment 14, 819-828.

52. Chang D.P.Y. and Hill R.C. (1980) Retardation of aqueous droplet evaporation by air pollutants. Atmospheric Environment, 803-807.

53. Shaw R.W., Jr., Stevens R.K., Bowermaster J., Tesch J.W. and Tew E. (1982) Measurements of atmospheric nitrate and nitric acid: the denuder difference experiment. Atmospheric Environment 16, 845-853.

54. Possanzini M., Febo A. and Liberti A. (1983) New design of high performance denuder for the sampling of atmospheric pollutants. Atmospheric Environment 17, 2605-2610.

55. Sjödin A. and Ferm M. (1985) Measurements of nitrous acid in an urban area. Atmospheric Environment 19, 985-992.